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A Method for Obtaining Depolarization Factors of Raman Lines, with Results for Carbon Tetrachloride and Toluene[1,2]

FORREST F. CLEVELAND
Department of Physics, Illinois Institute of Technology, Chicago, Illinois

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A method for obtaining depolarization factors of Raman lines is described in which a 90°, split-field Polaroid disk is placed in contact with the window of the Raman tube and is focused upon the slit of the spectrograph by means of a condensing lens. Corrections for real or apparent polarization owing to the spectrograph, reciprocity failure of the plates, and convergence errors are made. The precision of the results was tested by measurements on five different spectrograms of CCl_4. The results indicated that the method is equal in precision to the method of Reitz. Intensities were obtained by use of a Gaertner microdensitometer. Depolarization factors for toluene were also obtained. It is shown that, for this method, a reasonable working rule is to regard those Raman lines having observed depolarization factors equal to or greater than 0.78 as depolarized, all others as polarized.

INTRODUCTION

IN many cases it is possible to determine the structure of a molecule[3] by interpreting the Raman and infra-red spectra with the aid of the group theory selection rules[4] for two or more assumed structures. To do this, one must know how many lines are depolarized (depolarization factor $=\rho=6/7$) and how many lines are polarized ($\rho<6/7$). This requires very precise values for those depolarization factors whose values are near 6/7 in order to decide whether these lines are polarized or depolarized. With this in mind, the method previously used in this laboratory[5,6] has been revised with a view toward more precise results.

METHOD FOR SEPARATION OF THE HORIZONTAL AND VERTICAL COMPONENTS

If the incident light is in a vertical plane, the depolarization factor is the ratio of the intensity I_v corresponding to the vertical component of the electric vector, in the scattered beam, to the intensity I_h corresponding to the horizontal com-

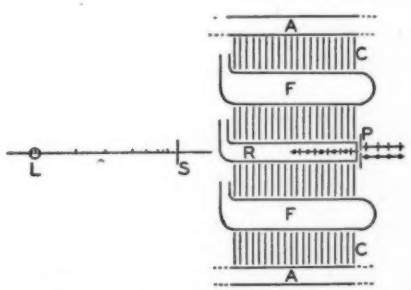

FIG. 1. Experimental arrangement for separating the horizontal and vertical components.

[1] Communication No. 42 from the *Spectroscopy Laboratory*.
[2] Presented at the Chicago meeting of the American Physical Society, December, 1944; abstract in Phys. Rev. 67, 62 (1945).
[3] See, for example, Dwight T. Hamilton and Forrest F. Cleveland, J. Chem. Phys. 12, 249 (1944).
[4] Cf. Arnold G. Meister, Forrest F. Cleveland, and M. J. Murray, Am. J. Phys. 11, 239 (1943).
[5] Forrest F. Cleveland and M. J. Murray, J. Chem. Phys. 7, 396 (1939).
[6] Forrest F. Cleveland, J. Chem. Phys. 11, 1 (1943).

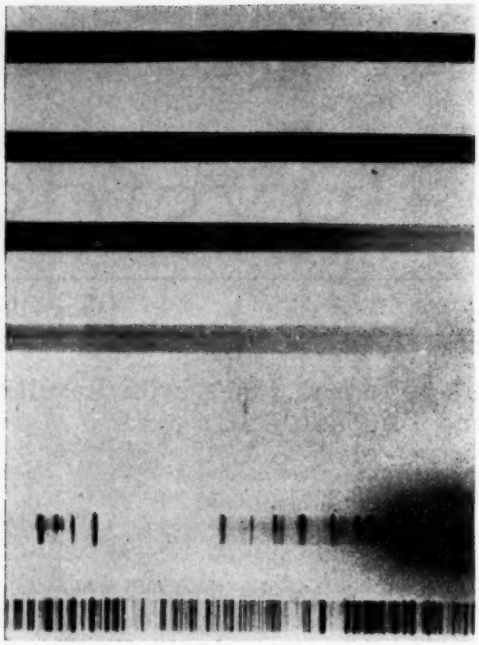

FIG. 2. Enlargement of a polarization spectrogram of toluene.

ponent of the electric vector, or $\rho = I_v/I_h$. The experimental arrangement for separating the horizontal and vertical components is shown in Fig. 1. A 90°, split-field Polaroid disk P is placed in contact with the window of the Raman tube R, in such a manner that the top part of the disk passes the vertical component, the lower part the horizontal component.[7] A condensing lens, not shown in Fig. 1, forms a sharp image of P on the slit of the spectrograph,[8] thus producing a sharp separation of the vertical and horizontal components, which appear one above the other on the photographic plate. Eastman 103-J plates were used, and the Raman spectra were produced by the Hg 4358A line. Thus, the Raman lines fall in the region 4400–5100A for which the polarizing properties of the Polaroid are good.

The incident light is made perpendicular to the scattered beam, as nearly as is feasible, by use of the blackened canals C. The width of the canals was 5 mm. Other dimensions were the same as in the previous method.[5] The mercury arcs A are placed in the vertical plane through the Raman tube because tests showed that this arrangement gave Raman lines of more nearly uniform density. The filter solution F was contained in cylindrical glass tubes and served to concentrate light from the arcs along the axis of the Raman tube. This makes it possible to obtain depolarization factors for otherwise immeasurable weak lines, but also requires a correction for convergence, as explained later.

By this method it was possible to obtain the lines corresponding to the horizontal and vertical components *simultaneously*, thus avoiding errors caused by variations in the intensity of the light source, changes in turbidity or coloring of the sample, changes in transmissivity of the filters, and other changes that might occur between or during exposures if the lines corresponding to the horizontal and vertical components were obtained in two, non-similtaneous exposures. Such simultaneous exposures are a necessity for precise results.

CALIBRATION MARKS

Another requirement for precise results is that calibration marks be placed on *each* plate and that calibration curves be prepared for *each* Raman line by plotting the densities of the calibration marks against the logarithms of the corresponding relative intensities.[9,10] In the present work, eight calibration marks were obtained upon each plate by placing a small incandescent lamp L at the points indicated in

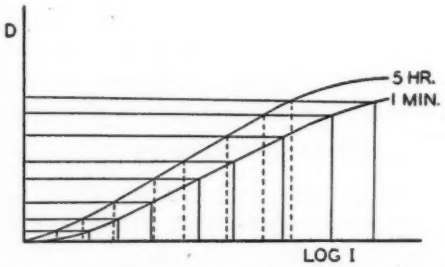

FIG. 3. Curves used in correcting for failure of the reciprocity law.

[7] Dr. Wilfried Heller suggests that it might be desirable to replace the Polaroid disk with two Glan-Thompson prisms.

[8] G. Glockler and H. T. Baker, J. Chem. Phys. **11**, 446 (1943) and G. Glockler, J. F. Haskin, and C. C. Patterson, J. Chem. Phys. **12**, 349 (1944), have recently described a simplified method in which the Polaroid was placed in front of the slit of the spectrograph. In this arrangement, the Polaroid must be in intimate contact with the slit in order to produce sharp separation of the vertical and horizontal components.

[9] Cf. G. R. Harrison, J. Opt. Soc. Am. **19**, 267 (1929).

[10] A. W. Reitz, Zeits. f. physik. Chemie **B33**, 368 (1936).

Fig. 1, the distances from the ground glass screen S being such that known relative intensities of illumination were produced upon the screen. The lamp was operated from a bank of six storage batteries in parallel to insure constant voltage across the lamp. The Raman tube R was removed during the calibration exposures; otherwise, the optical path was identical for the Raman and calibration exposures.

A reproduction of a polarization spectrogram of toluene is shown in Fig. 2. The top part of the Raman spectrum corresponds to the horizontal component, the bottom part to the vertical component. An iron arc spectrum appears below the Raman spectrum for use in identifying the Raman lines, and the calibration marks appear above the Raman spectrum. The calibration marks show polarization, real or apparent, caused by the spectrograph or by other optical parts in the path of the light beam. This was corrected for by determining the ratio of the intensities corresponding to the two areas on the calibration mark, for the three calibration marks that could be most reliably measured. Since this ratio must be unity, the correction factor that must be multiplied by the observed ρ value to correct for the real or apparent polarization of the spectrograph and its auxiliary optical parts could be readily obtained. This correction factor was determined for each of the Raman lines measured, but it was found that, within experimental error, the factor was the same for all values of the Raman displacements from 200 to 3000 cm^{-1} (4400 to 5100A). The mean value, 1.16, was therefore used in correcting the ρ value of each line for real or apparent polarization of the instrument. This was done by multiplying each observed ρ value by the correction factor, 1.16.

TABLE I. Depolarization factors for the Raman lines of carbon tetrachloride (CCl_4, liquid state), obtained from five different spectrograms.*

	Depolarization Factor, ρ							
			Plate			Mean		
$\Delta\nu$	244	245	246	247	248	ρ	a.d.	m.d.
217	0.846	0.875	0.868	0.858	0.818	0.853	0.017	0.035
313	0.870	0.850	0.914	0.851	0.851	0.867	0.020	0.047
459	0.144	0.144	0.030	0.027	0.016	0.072	0.057	0.072
760	0.875	0.877	0.811	0.833	0.839	0.847	0.023	0.036
791	0.867	0.908	0.818	0.754	0.815	0.832	0.044	0.078

* $\Delta\nu$ = Raman displacement in cm^{-1}; ρ = depolarization factor; a.d. = average deviation of a single observation from the mean value; and m.d. = maximum deviation of a single observation from the mean value.

TABLE II. Comparison of the results for the five different spectrograms of CCl_4 with the results obtained by Reitz for five different spectrograms.

	Present results			Reitz's results		
$\Delta\nu$	ρ	a.d.	m.d.	ρ	a.d.	m.d.
217	0.853	0.017	0.035	0.854	0.021	0.048
313	0.867	0.020	0.047	0.872	0.030	0.062
459	0.072	0.057	0.072	0.045	0.015	0.027
760	0.847	0.023	0.036	0.742	0.055	0.111
791	0.832	0.044	0.078	0.777	0.028	0.043
	Mean:	0.032	0.054	Mean:	0.030	0.058

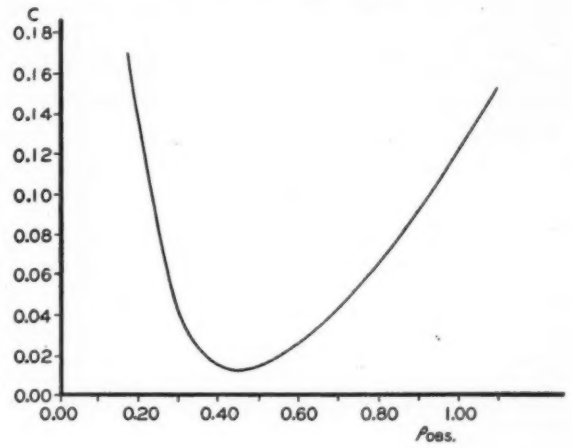

FIG. 4. Curve used in correcting for convergence errors.

CORRECTION FOR FAILURE OF THE RECIPROCITY LAW

Since the Raman exposures were 0.5 to 5 hours in duration and the calibration exposures were only one minute, it was necessary to correct for failure of the reciprocity law. The method whereby this was done is indicated in Fig. 3: The lower curve was obtained with one-minute exposures and with the relative intensities 1000, 500, 250, 100, 50, 20, 10, and 5, whose logarithms are indicated by the heavy vertical lines. The upper curve was obtained on the same plate with 5-hr. exposures. The logarithms of the relative intensities that would have had to have been used for 5-hr. exposures to produce the same densities as were obtained with the one-minute exposures are those indicated by the dashed vertical lines in Fig. 3, and these are the ones used in plotting the calibration curves.

Curves similar to those shown in Fig. 3 were obtained for 0.5-, 1-, and 5-hr. exposures for $\Delta\nu$

values of 200, 1450, and 3000 cm^{-1}. For intermediate times of exposure or for intermediate values of $\Delta\nu$, the corrections could then be obtained by graphical interpolation.

CORRECTION FOR CONVERGENCE ERRORS

The correction for convergence errors due to use of the cylindrical filters (F in Fig. 1) was made by use of the correction curve shown in Fig. 4. This curve was obtained by comparing

TABLE III. Comparison of the results of five independent determinations of the depolarization factor for the 217-cm^{-1} line of CCl_4 by the present method with the corresponding results obtained by Reitz.

	Present results				Reitz's results	
	Plate 244	a.d.	Plate 245	a.d.	Plate 191	a.d.
	0.864	0.020	0.874	0.016	0.830	0.001
	0.829	0.015	0.876	0.018	0.805	0.026
	0.857	0.013	0.844	0.014	0.835	0.004
	0.826	0.018	0.843	0.015	0.862	0.031
	0.843	0.001	0.855	0.003	0.825	0.006
Mean:	0.844	0.013	0.858	0.013	0.831	0.014
m.d.		0.020		0.018		0.031

TABLE IV. Comparison of the present results for CCl_4 with the results obtained by Reitz and Simons.

	Depolarization factors		
$\Delta\nu$	Present results	Reitz	Simons
217	0.853	0.854	0.88
313	0.867	0.872	0.93
459	0.072	0.045	0.05
760	0.847	0.742	0.87
791	0.832	0.777	

the results obtained for the stronger lines of toluene by the present method with the results obtained by Simons[11] by a more ideal, but much slower, method. The correction C is the amount that must be subtracted from the observed value of ρ, following the correction for real or apparent polarization of the spectrograph, to correct for convergence errors. The correction is greater for large and small values of ρ and less for intermediate values of ρ.

RESULTS WITH CCl_4 FOR FIVE DIFFERENT SPECTROGRAMS

To test the precision of the method, five polarization spectrograms of CCl_4 were made, as Reitz[10] had done in testing the precision of his method. The intensities were obtained by use of a Gaertner microdensitometer, and correction for the continuous background was made as described previously.[6] Five readings of the microdensitometer were taken for each setting on the Raman line and on the calibration marks for each determination of the value of ρ. Two independent determinations of ρ were made for each Raman line; and if these differed by more than 0.05, a third determination was made. The mean of these two, or three, values was taken as the final value of ρ. The final results so obtained for the five different spectrograms, corrected for real or apparent polarization of the spectrograph and for convergence errors, are given in Table I.

A comparison of the final results by the present method with the results obtained in the similar test by Reitz is made in Table II.

In order to find how much of the error is caused by the microdensitometer, five independent determinations of ρ were made on the 217-cm^{-1} line for each of two different plates. The results are compared with the results of a similar test by Reitz in Table III. It is evident from this table that a considerable part of the error, perhaps half of it, is caused by the microdensitometer, or in Reitz's work by the microphotometer. Since the errors of setting are random errors, the reliability of the ρ values could be increased by making a

TABLE V. Depolarization factors for toluene (methylbenzene, C_7H_8, liquid state).

		Depolarization factors	
$\Delta\nu$	I*	Present method	Simons
217	8*b*	0.92	0.91
521	7	0.44	0.34
622	4	0.85	0.85
785	12	0.03	0.10
1002	12	0.13	0.07
1032	6	0.11	0.27
1153	3	0.87	0.88
1176	1	0.85	—
1209	8	0.29	0.25
1377	3	0.46	0.42
1580	1	0.85	0.92
1603	5*b*	0.84	
2867	3*b*	0.15	—
2917	10*b*	0.23	0.29
3055	10*vb*	0.33	0.34

* Data for the Raman frequencies from K. W. F. Kohlrausch and A. Pongratz, Sitz. Akad. Wiss. Wien [IIb] **142**, 637 (1933); weak lines for which depolarization factors were not obtained are not included; I = estimated intensity, *b* = broad, *vb* = very broad.

[11] L. Simons, Soc. Sci. Fenn. Com. Phys. Math. **6**, No. 13 (1932).

greater number of independent settings. One could first determine the ρ values by the aforedescribed method, then make additional determinations for those lines having observed ρ values equal to or greater than 0.70. For cases in which clear-cut conclusions can be expected from the polarization data on the basis of such increased reliability of the results, the considerable additional labor might be justified.

From the results given in Tables II and III, it seems possible to conclude that the present method is equivalent in precision to Reitz's method. It appears from a comparison of the results of Simons[11] with the present results and with those of Reitz, Table IV, that the values of ρ obtained by Reitz for the 760- and 791-cm^{-1} lines may be somewhat too low.

RESULTS FOR TOLUENE

Since the depolarization factors obtained by Simons for the stronger lines of toluene were used to get the values of the correction factors for convergence that were used in the present method, the values obtained for these lines in the present investigation should be the same as those obtained by Simons. However, because of experimental errors, the individual values will not agree exactly. The degree of correlation obtained may be seen from Table V in which the values obtained by the present method are listed alongside those of Simons. In general the agreement between the two sets of values is good; however, the value of 0.27 given by Simons for the 1032-cm^{-1} line seems to be too large. Also Simons reported a ρ value of 0.74 for a line at 2984 that was not observed in the present investigation and was also not observed by Kohlrausch and Pongratz whose frequency and intensity values are used in Table V. Depolarization factors were obtained for the 1176- and 2867-cm^{-1} lines for which Simons reported no values, and depolarization factors were obtained for each of the components of the 1580, 1603 doublet that was unresolved in the work by Simons.

WHICH LINES ARE DEPOLARIZED?

Having established the precision of the results obtainable by the present method, it is now necessary to decide which lines shall be taken as depolarized ($\rho=6/7$) and which lines shall be taken as polarized ($\rho<6/7$). This is difficult since it is not possible to prove experimentally that any Raman line has a ρ value of *exactly* 6/7 because of the experimental error involved.

A perhaps not too unreasonable approach to the problem is the following: In the present rather exhaustive measurements of the ρ values of CCl_4, the two largest deviations of a single value from the mean were 0.078 and 0.072. (For comparison, the corresponding values in Reitz's results were 0.111 and 0.062.) One can thus consider it to be improbable that a depolarized line would have a ρ value less than $0.86-0.08=0.78$, although this is certainly not impossible, especially for cases in which the intensity of the continuous background approximates that of the line or for cases in which two lines fall very close together. Thus, there is some possibility that a depolarized line might have an observed ρ value less than 0.78.

On the other hand, there is the possibility that Raman lines having true ρ values in the range 0.70 to 0.85 might yield observed ρ values equal to or greater than 0.78. However, this may not be too probable, because in molecules possessing symmetry only the totally symmetrical vibrations are polarized; and, moreover, if an axis of symmetry is present, these vibrations usually correspond to Raman lines having small ρ values. All vibrations that are degenerate or that are antisymmetrical with respect to any element of symmetry, if not forbidden, are depolarized.[12] Furthermore, the ρ values of the lines that are polarized can fall anywhere within the rather large range 0.00 to 0.85. Hence the probability that a polarized line would have an observed ρ value equal to or greater than 0.78 would appear to be quite small and would tend to compensate for the small chance that a depolarized line might yield an observed ρ value less than 0.78.

It thus appears that a reasonable working rule for the present method would be to consider those Raman lines having observed ρ values equal to or greater than 0.78 to be depolarized

[12] See the article by G. Placzek in *The Structure of Molecules* (P. Debye), (Blackie and Son, Ltd., London, 1932), p. 79.

and those having observed ρ values less than 0.78 to be polarized.

ACKNOWLEDGMENTS

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The Measurement of Potentials at the Interface Between Vitreous Silica and Solutions of Potassium Chloride by the Streaming Potential Method*

GRINNELL JONES[1] AND LLOYD A. WOOD
Department of Chemistry, Harvard University, Cambridge, Massachusetts

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Improvements in the technique for the determination of the electric potential at the interface between a non-conducting solid and an aqueous solution of an electrolyte (commonly called the zeta-potential) have been developed and are described in detail. Zeta-potentials of vitreous silica capillaries in contact with three dilute solutions of potassium chloride (10^{-3}, 10^{-4}, $10^{-5}N$) have been determined. These data have been used for the interpretation of the surface tension data of Jones and Ray by using Langmuir's theory for the thickness of wetting films as a function of the zeta-potential.

INTRODUCTION

JONES and Ray[2] have made measurements of capillary rise of water and of solutions of electrolytes in the same silica tube which showed that the first trace of added salt decreases the capillary rise and the product of the density and capillary rise which is the so-called "capillary constant"; but that with further additions of salt the capillary constant passes through a minimum and then rises (although not an increase in the capillary rise). Their interpretation was that there is a minimum in the surface tension-concentration curve at about $0.001N$. Thirteen salts of varied valence type give the effect, but sucrose does not. However, Langmuir[3] has suggested an alternative interpretation of these observations, that the apparent minimum in the surface tension is not real but is a result of a variation in the thickness of the wetting film which influences the effective diameter of the tube. The theory is developed in a somewhat more rigid mathematical form, and its implications are discussed by Jones and Frizzell.[4] According to Langmuir's hypothesis, this film with pure water and with extremely dilute solutions is not negligible in comparison with the radius of the capillary, as has been assumed by all experimenters using the capillary rise method, but may be several hundred angstrom units thick. The thickness of the wetting film of solutions of electrolytes, according to Langmuir's theory, is

* Contribution from the Mallinckrodt Chemical Laboratory of Harvard University.

[1] The preliminary work on the development of the apparatus and technique was carried out by Mr. Harvey S. Collins under the supervision of the senior author. Mr. Collins' work made it evident that a potentiometer and detector of very high internal resistance must be used, that silver-silver chloride electrodes are preferable to platinum electrodes used by many other investigators, and that the previous history of the capillaries plays a significant role and must be controlled as fully as is feasible. Mr. Collins found it necessary to terminate his work before the improved technique was developed and publishable results were obtained. We wish to express our appreciation for his contributions to the work described here.

[2] G. Jones and W. A. Ray, J. Am. Chem. Soc. **59**, 187 (1937); **63**, 288 (1941); **63**, 3262 (1941); **64**, 2744 (1942).

[3] Irving Langmuir, Science **88**, 430 (1938); J. Chem. Phys. **6**, 894 (1938).

[4] G. Jones and L. D. Frizzell, J. Chem. Phys. **8**, 986 (1940).

dependent mainly on the potential at the interface between the wall of the capillary and the water or solution, commonly called the zeta-potential, but also on the concentration of the solution, the temperature, and the capillary rise (which in turn depends upon the radius of the capillary and the surface tension of the liquid). The zeta-potential itself may be dependent on the temperature, the chemical nature and concentration of the electrolyte, the chemical nature of the capillary (glass or vitreous silica), and perhaps on its previous history which may influence the amount and nature of adsorbed ions. According to this theory the thickness of the wetting film is greatly influenced by the concentration of electrolyte within the range from 0 to about $0.01N$ (unless there are compensating changes in the zeta-potential). If the wetting film for water is thicker than for $0.001N$ solution by as much as 250 angstrom, the data on capillary rise could be interpreted without inferring that there is a minimum in the surface tension-concentration curves.

In the Langmuir theory the zeta-potential plays a controlling role. In order to make quantitative tests of this theory, it is necessary to have reliable data on the magnitude of these zeta-potentials. Significant improvements in the technique of measuring zeta-potentials are described in this paper.

Moreover, the Langmuir theory assumes that the charge at the air-solution interface is zero, although there are in the literature experimental observations of several kinds which have been interpreted by the experimenters as proof that solutions at an air-solution interface are electrically charged.[5] A paper developing a modification of the original theory so as to take into account a charge on the solution-air interface is in preparation. However, the quantitative testing of the modified theory will require reliable measurements of the potential at air-solution interfaces which are not available and which will be extremely difficult to determine experimentally, as well as measurement of potentials at solid-solution interfaces commonly called the zeta-potential.

Dole and Swartout[6] have developed a twin-ring tensiometer which is capable of high precision and have found a minimum in the surface tension-concentration curve for potassium chloride solutions at $0.001N$, in agreement with Jones and Ray. On the other hand, Long and Nutting,[7] using an improved differential bubble pressure method, do not find a minimum in the curve.

MEASUREMENT OF ZETA-POTENTIALS—GENERAL REQUIREMENTS

Zeta-potentials may be computed from four different electrokinetic effects: streaming potentials, electro-osmosis, sedimentation potentials, and electrophoresis—provided that certain other necessary data are available. The method based on streaming potentials lends itself most readily to precision measurement, since all of the quantities involved in the computation are measurable with greater accuracy and less difficulty than the fundamental experimental data for the other three methods.

A streaming potential is the potential difference which develops between the ends of a capillary tube when a solution of an electrolyte (including the purest available water which contains enough ions to produce the effect) is forced through the tube by external pressure or by gravity. If the flow is slow enough to be streamlined, so that Poiseuille's law is applicable, this potential is related to the zeta-potential at the wall of the tube by the equation of Helmholtz:[8]

$$\zeta = 4\pi\eta\kappa E/DP, \qquad (1)$$

where η is the viscosity, K is the specific conductance of the liquid in the capillary, E is the streaming potential resulting when the liquid is forced through the capillary under the pressure P, and D is the average dielectric constant of the liquid in the ionic double layer.

[5] H. A. McTaggart, Phil. Mag. [5] **27**, 297 (1914); N. Bach and A. Gilman, Acta Physicochimica U.R.S.S. **9**, 1 (1938); P. Lenard, Ann. d. Physik [4] **47**, 463 (1915); W. Obolensky, *ibid.* [4] **39**, 961 (1912); W. Busse, *ibid.* [4] **76**, 493 (1925); A. Bühl, *ibid.* [4] **83**, 1207 (1927); *ibid.* [4] **84**, 211 (1928); *ibid.* [4] **87**, 877 (1928); Kolloid Zeits. **59**, 346 (1932); F. B. Kenrick, Zeits. f. physik. Chemie **19**, 625 (1896); **109**, 34 (1924); **111**, 190 (1924); **116**, 485 (1925); see also H. Freundlich, *Kapillarchemie* (Leipzig, 1930), fourth edition, Vol. 1, pp. 388–399, which gives many additional references.

[6] M. Dole and J. A. Swartout, J. Am. Chem. Soc. **62**, 3039 (1940).

[7] F. A. Long and G. C. Nutting, J. Am. Chem. Soc., **64**, 2476 (1942).

[8] H. Helmholtz, Wied. Ann. **7**, 337 (1879).

Several experimenters[9] have measured zeta-potentials by the streaming method, mostly on glass capillaries, but there are also some measurements on vitreous silica capillaries. However, nearly all data on comparable systems are greatly at variance, and it is difficult to evaluate their relative reliability for several reasons. Several different varieties of glass, some entirely unspecified, have been used for these determinations, which therefore could hardly be expected to be in

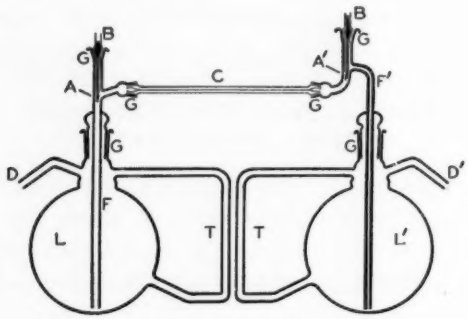

FIG. 1.

agreement. It is most unfortunate that the investigators did not choose silica or some other pure substance rather than a mixture of such indefinite composition as glass as a subject for study. Some experimenters have failed to appreciate the importance of, or to describe adequately, the previous history and treatment of the solid surfaces. Measuring instruments have been used which are unsuitable for measuring such a delicate effect as the streaming potential or have not been described sufficiently to permit a critical appraisal of their suitability. The conductance of solutions used has in some cases not been determined but the values for κ used in the calculations were taken from the literature. However, since the solutions used are commonly quite dilute (less than $0.001N$) the undetermined and uncertain "water correction" may introduce a substantial error in the assumed value of κ, and hence in ζ. The possible influence of surface conductance on streaming potentials has commonly been neglected. It is evident from a survey of the literature that most of the data are unreliable, and it is difficult to determine which, if any, are worthy of confidence. Therefore it was thought advisable to undertake an investigation for the purpose of improving the experimental technique of measuring streaming potentials and the other necessary quantities, and thus obtain some reliable data which can be used to test the Langmuir theory.

From Eq. (1) it is evident the apparatus required for measuring zeta-potentials must include devices for measuring the streaming potential, the pressure producing the liquid flow, and the specific electrical conductivity of the solution used in the capillaries. The viscosity of the solutions used are nearly the same as water, and sufficiently reliable data are available in the literature. The dielectric constant of the solutions is assumed to be the same as that of water.

DESIGN OF STREAMING APPARATUS AND DRIVING PRESSURE

The apparatus for developing streaming potentials consisted essentially of two Pyrex reservoirs of 1-liter capacity, L and L' in Fig. 1, connected by a vitreous silica capillary C. Pressure applied from a nitrogen tank through D on one side forced the solution through the tube F, around the electrode A, through the capillary C, around the other electrode A', and finally into the opposite reservoir L'. The tubes were so designed that pressure in L forced all air bubbles out through L' which accounts for the lack of symmetry shown in the diagram. The delivery tube F' is a capillary of about 1-mm bore which is small enough so that air bubbles will be forced down the tube. After the initial filling the direction of flow may be reversed. The tight fitting ground joints G connecting the various parts of the apparatus were sealed with a minimum of paraffin, which was not surface active and was kept on the outward half of the joints as much as possible. The capillary C was about 19.1 cm long and 0.032 cm in diameter. A second apparatus, differing slightly in detail, was in use simultaneously with a capillary 19.2 cm long and 0.017 cm in diameter.

[9] H. R. Kruyt and van der Willigen, Kolloid Zeits. **45**, 307 (1928); Furutani, Kurokochi, and Asoda, Jap. J. Gastroent. **2**, 148 (1930); H. Freundlich and G. Ettisch, Zeits. f. physik. Chemie **116**, 401 (1925); H. Lachs and J. Biczyk, Zeits. f. physik. Chemie **A148**, 441 (1930); R. DuBois and A. H. Roberts, J. Phys. Chem. **40**, 543 (1936); A. J. Rutgers, Trans. Faraday Soc. **36**, 69 (1940); A. J. Rutgers, Ed. Verlende, and MaMoorkens, Proc. K. Ned. Akad. Wet. Amst. **41**, 763 (1938).

For measurements of the pressure difference applied between L and L', a mercury manometer was satisfactory for the range required, from 15 to 35 cm of mercury. Constancy of pressure was maintained through the use of large ballast reservoirs covered with heat lagging on both the pressure and exhaust sides of the apparatus. The tubes T permitted a measurement of the difference in hydrostatic head between the reservoirs which was applied as a small correction to the measured gas pressure.

The Helmholtz equation for the calculation of zeta-potentials is based on the assumption that the flow in the capillary is stream-lined and obeys Poiseuille's law.

With the larger of our two capillaries (diameter 0.032 cm) and with the highest pressure used (35 cm of Hg) the rate of flow is 0.07 cc/sec., and the Reynolds number is 310. For the smaller of our capillaries and the greatest velocity the rate of flow is 0.0056 cc/sec., and the Reynolds number is 48. These Reynolds numbers are well below the critical value of 2000 for the Reynolds number which indicates danger of turbulence.[10]

MEASUREMENT OF STREAMING POTENTIAL AND TEMPERATURE CONTROL

The electrodes A were spirals of No. 28 gauge platinum wire on which a silver-silver chloride mixture was formed by heating a paste of 10 percent silver chlorate-90 percent silver oxide mixture at 500° for 15 minutes.[11] The platinum wires supporting the silver-silver chloride electrodes were sealed through glass which permitted them to be connected to the measuring instruments by copper wires dipping into the mercury cups B.

It was necessary to apply rather elaborate electrical insulation and electrostatic shielding to the capillary apparatus and one of the connecting wires to the potentiometer, owing to the separation of this part of the electrical system from the remainder by the extremely high resistance of the capillary and the still higher resistance of the vacuum tube in the null instrument of the potentiometer. In order to take advantage of air insulation, the apparatus was enclosed in an air thermostat rather than a liquid bath. This thermostat was designed essentially in the manner of one constructed by Mr. E. B. Damon of the Mallinckrodt Chemical Laboratory.[12] An inner chamber entirely shielded with a grounded copper sheet or a 16 mesh wire screen, with a removable glass door in front and an illuminated pane of frosted glass in the rear, contained the two units of capillary apparatus which were essentially duplicates except for the capillaries which differed appreciably in diameter as explained above. The inner chamber was mounted inside an outer larger cabinet with walls of low heat conductivity and also provided with glass windows to permit inspection of the apparatus in the inner chamber. The temperature of the air in the outer chamber was automatically maintained at the desired value by a low lag intermittent electric heater

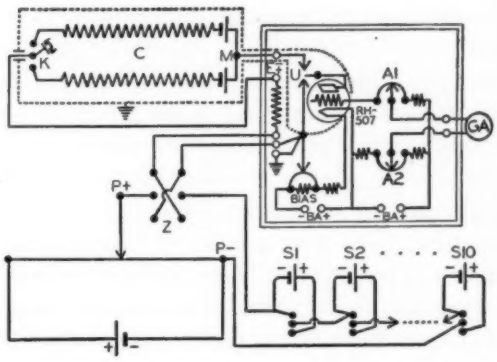

FIG. 2.

controlled by a sensitive metallic spiral. Occasionally when the room temperature was high enough to require it, constant cooling was applied by circulating cold water through some copper coils in the outer chamber. A small fan circulated the air over the heater, regulator, drying agent,

[10] O. Reynolds, Phil. Trans. **174**, 935 (1883); **A186**, 123 (1895). See also E. C. Bingham, *Fluidity and Plasticity* (McGraw-Hill Book Company, Inc., New York, 1922), p. 40. It should be noted that in his first paper Reynolds defines his criterion (a dimensionless number) in terms of the radius $Re=ru\rho/\eta$ where r=radius of capillary; u is mean velocity of flow, cm/sec., averaged over the cross section; ρ is the density of the liquid; and η is the viscosity of the liquid. Bingham in his book uses this definition. However, in his second paper Reynolds defines his criterion in terms of the diameter of the tube $Re=Du\rho/\eta$ where $D=2r$. We have used this definition because it is customarily used in books on chemical engineering and is therefore more familiar.

[11] C. K. Rule and Victor K. LaMer, J. Am. Chem. Soc., **58**, 2339 (1936).

[12] Mr. Damon has not published a description of this air thermostat. We wish to express our thanks for permission to use his design and publish this description of it.

and around the inner chamber. Suitable partitions were built into the apparatus to ensure that the air circulated all around the inner chamber and that a small part of the circulating air passed through the inner chamber. The inner chamber also contained open dishes containing a drying agent (calcium chloride) to maintain the humidity at a low value. The temperature in the inner chamber was maintained at 25°C±0.03°. This thermostat has the unavoidable drawback that owing to its low heat capacity a long wait is necessary after opening the chamber to change the solution or for any other purpose, before adequate temperature control is established so that measurements can be made.

The capillary apparatus was mounted on glass plates without metal supports, and the connecting wires from the electrodes to M and K (Fig. 2) were air insulated. The wire from M to the $E-$ terminal of the amplifier passing through the walls of the thermostat was a length of coaxial cable with polystyrene beads for insulation and a grounded metallic braided shield. The knife switch K, with contacts mounted in a block of paraffin, was controlled from the outside of the thermostat by a Bakelite rod and made possible alternate measurements with either set of capillary apparatus. The reason for the paraffin insulation is made apparent by recalling that the positive terminals of both capillaries were connected to the terminals of this switch. Since the resistance of ordinary porcelain switches when open is in some instances low compared with that of the capillary the effect would be that of a closed circuit through both capillaries. It is believed that these insulation precautions have ensured that the resistance of all electrical paths between the electrodes other than through the capillary was greater than 10^{13} ohms.

The potential difference between the electrodes was measured with a Wolff potentiometer having a resistance of 19,000 ohms. The proper choice of the null instrument is important because Eq. (1) assumes that the electrical current which escapes through the measuring instrument or by other leakage owing to inadequate insulation is negligible, i.e., is so small that it does not permit the discharge of the electrodes to a significant extent. Many previous investigators have used galvanometers or capillary electrometers which did not satisfy this requirement. In practice this requirement may be met by ensuring that the losses will be negligible in comparison with the magnitude of E/R, where E is the streaming potential and R the resistance of the capillary. The resistance may be as high as 10^{10} ohms and the streaming potential as low as 100 millivolts in extreme circumstances, giving a minimum value of E/R of 10^{-11} ampere. In this work a Leeds and Northrup thermionic amplifier (Cat. No. 7673) was used as a null instrument, which permits a leak of not more than 10^{-13} ampere, and gives streaming potential measurements which are sensitive to better than 0.5 percent in the most difficult cases and to 0.1 percent or better in the more favorable cases.

The potentiometer circuit is shown diagrammatically in Fig. 2, including the thermionic amplifier. A brief explanation of this instrument will be helpful, and further information is available elsewhere.[13] The vacuum tube of the amplifier (R.H.-507, Westinghouse electrometer tube) is so designed that with correct adjustment of the bias voltage less than 10^{-13} ampere of electron current flows from filament to plate which is in series with the capillary. The filament-to-grid flow is incorporated in one arm of the bridge which is a part of the electrical system of the instrument and which can be balanced by adjusting the resistors $A1$ and $A2$, so that a galvanometer across the midpoints will give a null reading for some definite value of the filament-to-grid potential difference. Since this difference depends upon the potential of the plate, the galvanometer is really actuated by the potential difference between filament and plate.

In the diagram (Fig. 2) it is assumed that the direction of flow in the capillary is such that the end marked M is positive. In measuring the streaming potential, the switch U was first depressed, which connected the plate to ground and to the positive side of the potentiometer ($P+$), the switch Z being in such position that the positive side of the potentiometer is grounded. The resistors $A1$ and $A2$ were then adjusted so that when the plate was at ground potential, the

[13] *Directions for No. 7673 Thermionic Amplifier* (Leeds and Northrup Company, Philadelphia, Pennsylvania); R. H. Cherry, Trans. Am. Electrochem. Soc. **78**, 11 (1940); Müller, Gorman, and Droz, *Experimental Electronics* (Prentice-Hall, Inc., New York, 1942), p. 168.

filament-to-grid potential difference was such that the galvanometer was not deflected. Then switch U was released, and the plate assumed the potential of the positive electrode of the capillary (represented diagramatically in Fig. 2 by C). The negative end of the capillary was connected through the knife switch K to $E+$, which in turn connected through a low resistance to $P-$, the negative side of the potentiometer. By adjusting the potentiometer until its potential was equal and opposite to the streaming potential, the potential of the plate was returned to ground potential. This state of affairs was indicated by the return of the galvanometer to null reading. Thus the streaming potential is obtained.

When the direction of liquid flow was reversed, the polarity of the electrodes was also reversed, and it was necessary to have switch Z changed so that the negative side of the potentiometer was connected to ground. When the streaming potentials exceed the 1.9-volt range of the potentiometer, the Weston standard cells $S1$ to $S10$ were placed in series with the potentiometer to extend the range to 12 volts. The e.m.f.'s of these cells were checked individually with the potentiometer through another circuit not shown.

SPECIFIC CONDUCTIVITY OF SOLUTIONS USED

Most investigators have assumed the electrical resistance of the capillary to be determined by the geometry of the capillary and by the bulk conductance of the system. McBain and co-workers[14] have published evidence indicating that the specific conductance of the layer near the surface of the glass interface is greater than the specific conductance of the portion of solution at a greater distance from the interface. The excess of the actual conductance over the bulk conductance is called the surface conductance. If this is correct the value of the specific conductance determined in tubes of comparatively large diameter, such as the conventional conductivity cells, would be lower than the effective specific conductance in a narrow capillary tube. The error introduced in this way would be a function of the concentration of the solution—decreasing with increase in concentration. However, White, Urban, and co-workers[15] have obtained contradictory results. Rutgers, Verlende, and Moorkens[16] believing that surface conductance is appreciable, have measured streaming potentials with glass capillaries of different sizes and have calculated zeta-potentials and surface conductances from these, on the assumption that the zeta-potentials of the different capillaries are identical. However, since zeta-potentials are hard to reproduce and are apparently influenced by the previous history of the tube, this assumption is somewhat uncertain. Their results are in good agreement with McBain's. In view of this uncertainty existing as to the effect of surface conductivity, it was believed desirable to measure the conductance of the solution in the capillary at the time of each streaming potential measurement. Furthermore, since a trace of impurities produces a relatively large effect on the electrolyte concentration of extremely dilute solutions, this measurement also could give warning of the accumulation of impurities, mainly carbon dioxide. If the surface conductance plays a significant role in these measurements then the actual conductance of the capillary ($1/R$) will be given by the equations

$$\frac{1}{R}=\frac{\pi r^2}{l}\kappa_B+\frac{2\pi r}{l}\kappa_s, \tag{2}$$

$$\frac{l}{\pi r^2 R}=\kappa_B+\frac{2\kappa_s}{r}=\kappa_B\left(1+\frac{2\kappa_s}{\kappa_B r}\right)=\kappa, \tag{3}$$

where κ_B is the bulk specific conductivity and κ_s is the surface specific conductivity and κ is the total effective specific conductivity which is needed for insertion in Eq. (1). Therefore, if the cell constant, $l/\pi r^2$, can be determined with sufficient precision in a manner which avoids errors owing to surface conductance, then the effective specific conductivity, κ, can be computed from the measurements of the actual resistance (R) in the capillaries.

[14] McBain, Peaker, and King, J. Am. Chem. Soc. **51**, 3294 (1929); J. W. McBain and C. R. Peaker, J. Phys. Chem. **34**, 1033 (1930); J. W. McBain and J. F. Foster, J. Phys. Chem. **39**, 331 (1935).

[15] White, Urban, and Krick, J. Phys. Chem. **36**, 120 (1932); White, Urban, and van Atta, J. Phys. Chem. **36**, 3152 (1932); White, Urban, and Monaghan, J. Phys. Chem. **45**, 560 (1941).

[16] A. J. Rutgers, Trans. Faraday Soc. **36**, 69 (1940); Rutgers, Verlende, and Moorkens, Proc. K. Ned. Akad. Wet. Amst. **41**, 763 (1938).

According to McBain, Peaker, and King,[14] the ratio κ_s/κ_B decreases rapidly with increasing concentration. It is also clear that the difference $\kappa-\kappa_B=2\kappa_s/r$ decreases with increasing diameter of the cell and is generally assumed to be negligible for cells of the conventional non-capillary design. The procedure for the determination of the cell constant and the estimation of the influence of the surface conductance was as follows: An approximately $0.1N$ KCl solution, whose specific conductivity at 25°C, $\kappa_B=0.012798$, was known by comparison with the Jones and Bradshaw[17] standards, was placed in the capillary cells and the resistance measured with direct current on the special bridge described below. The resistances in these capillaries are so great that errors owing to capacitive by-paths make the usual procedure using alternating current inapplicable and errors due to polarization with direct current are minimized. Then assuming as a first approximation that for this comparatively high concentration $2\kappa_s/\kappa_B r$ is negligible in comparison with unity, the cell constants, $l/\pi r^2=\kappa R$, are computed. The length of the capillary l can be measured within about 0.1 cm (the uncertainty is owing to the somewhat flaring or trumpet shaped ends) and hence the radius of the capillary can be computed (assuming that the capillaries have a circular cross section and are uniform in radius throughout their length). The results are shown in Table I. Then solutions of 10^{-3}, 10^{-4}, and $10^{-5}N$ KCl were prepared and placed in the capillaries for the zeta-potential measurements and the resistance (R) measured while the fluid flow was in progress as described below, and the effective specific conductance, κ, including the surface conductance computed by the equation $\kappa=l/\pi r^2R$. Then, in order to determine whether or not the surface conductance made a significant contribution to the conductance, the bulk conductance κ_B of the same solution was determined in a conventional non-capillary cell by the use of alternating current on a Jones bridge and the apparent surface conductivity computed

$$\kappa_s=[(\kappa-\kappa_B)/2]r. \qquad (4)$$

The results are shown in Table II.

TABLE I. Data on capillaries used.

Capillary	Resistance megohms	Cell constant	Length cm	Radius cm
I	1.826±0.001	23365	19.1	0.01613
II	6.792±0.005	86920	19.2	0.00837

The values of the apparent specific surface conductivity are so small and erratic as to be within the limit of error of these measurements and indicate that (except possibly for the $10^{-5}N$ solution) the influence of surface conductance on our measurements of zeta-potential is negligible. In this respect our results are in agreement with White, Urban, and associates. However, our method of measuring the specific conductivity with a direct current bridge in the capillary itself during the flow of the liquid includes the effect of surface conductance, if any, on the zeta-potential measurements. Since the value of κ_s/κ_B decreases with increasing concentration, our original assumption that the influence of surface conductivity can be neglected when working with $0.1N$ KCl is justified.

Although the indicated surface conductivity in our measurements are much below the values obtained by McBain, Peaker, and King, we do not regard our results as necessarily inconsistent or contradictory with theirs because the experimental conditions are different in several respects. In our experiments the solutions were flowing at a rate of 32 to 85 cm per second averaged over the cross section of the capillary for the larger tube, depending upon the pressure used, and from 10 to 25 cm per second for the smaller tube. Although Reynolds' criterion indicates that the flow is straight-lined instead of turbulent in the sense that these terms are used in discussions of fluid

TABLE II. Data on surface conductivity.

Concentration	Capillary	κ_B ×10⁶	R megohms	$\kappa=l/\pi r^2R$ ×10⁶	$\kappa-\kappa_B$ ×10⁶	$\kappa_s=[(\kappa-\kappa_B)/2]r$ ×10⁶
10^{-3}	I	151.4	154.9	150.8	−0.6	−0.0048
	I	147.6	159.1	146.9	−0.7	−0.0056
	II	151.4	574.4	151.3	−0.1	−0.0004
	II	148.3	585.8	148.4	+0.1	+0.0004
10^{-4}	I	15.66	1488	15.70	+0.04	+0.00032
	II	15.08	5618	15.47	+0.39	+0.0017
10^{-5}	I	2.243	9765	2.393	+0.15	+0.0012
	II	2.851	29500	2.946	+0.10	+0.0004

[17] Grinnell Jones and B. C. Bradshaw, J. Am. Chem. Soc. **55**, 1780 (1933).

flow, nevertheless there may be sufficient disturbance of the ionic distribution to reduce the surface conductance in comparison with stationary conditions which prevailed in McBain's experiments. Moreover, we used direct current instead of alternating current, and our capillaries were vitreous silica whereas theirs were made of glass which may be expected to differ from silica in its tendency to emit ions into the surface layer of the solution.

To make possible such measurements, a direct current bridge was built capable of measuring resistances in the range 10^5 to 10^{11} ohms with a precision of 0.5 percent, or better, under optimum conditions. The wiring diagram of this bridge is shown in Fig. 3. The Wolff potentiometer without working battery was used as the variable resistor R_3, adjustable in steps of 0.1 ohm, with the range 0.1 to 19,000 ohms (although the range below 100 ohms was not used). The resistance coils of the potentiometer were calibrated against Bureau of Standards calibrated resistors with a Mueller bridge and found to be close enough to their nominal values to make corrections unnecessary. The resistance R_4 was a Type W W2 precision wire-wound resistor of 1 megohm resistance (± 0.1 percent) manufactured by the International Resistance Corporation of Philadelphia. The resistance R_1 of 10^7 ohms consisted of ten of these megohm resistors connected in series. Both R_1 and R_4 were calibrated at 25°C against the variable resistor and the two Bureau of Standards calibrated resistors of 100 and 10,000 ohms, and were close enough to their nominal values to make a correction unnecessary. It, therefore, seems probable that the errors in these resistors could not be responsible for an error of more than 0.1 percent of the true value of the capillary resistance when calculated from $R_2 = R_1R_4/R_3$.

With the resistors constituting the bridge, unknown resistances in the range 5×10^8 to 10^{11} ohms could be measured to 0.1 percent insofar as the limitations imposed by the resistors are concerned. By substituting a 10,000-ohm resistor for the megohm at R_4, the range between 5×10^6 and 10^9 ohms could be measured, and if a 1000-ohm resistor is used at R_4 the range is dropped to 5×10^5 to 10^8 ohms. As a null instrument, the thermionic amplifier was connected across the midpoints of the bridge, with the $P+$ and $P-$ terminals short-circuited. It was well suited for this purpose because a bridge in which the resistances were so large and with great inequalities of the arms requires that the null instrument have an extremely high internal resistance.

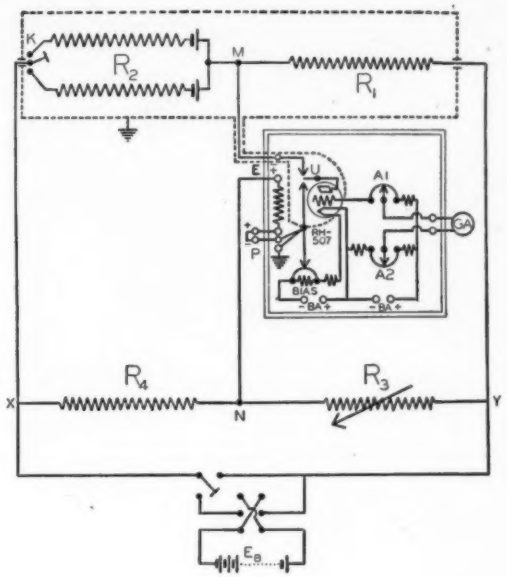

FIG. 3.

The same shielding and insulation precautions as described above were observed on the high resistance side, the arms R_1, R_2, and R_4 being inside the air thermostat where the air was maintained at low humidity to avoid surface leakage. The bridge current was supplied by B batteries at E_B, and because of the inequality of the bridge arms, potentials as high as 250 volts were used to obtain the necessary sensitivity. With no solution flowing through the capillary the streaming potential is zero, and except for a possible disturbance due to the small difference between the two silver-silver chloride electrodes, the bridge functions in the normal manner as a direct current bridge with resistance of the cell R_2 computed from the usual condition of balance $R_2 = R_1R_4/R_3$. Since the battery voltage is of the order of 250 volts the slight voltage, if any, in arm R_2, owing to asymmetry of the electrodes or polarization is negligible. Since the resistance of the capillary in the work reported here is within the range 2×10^6 to 4×10^{10} ohms and is in series with 10^7 ohms in R_1, direct current may be used without serious trouble from polarization.

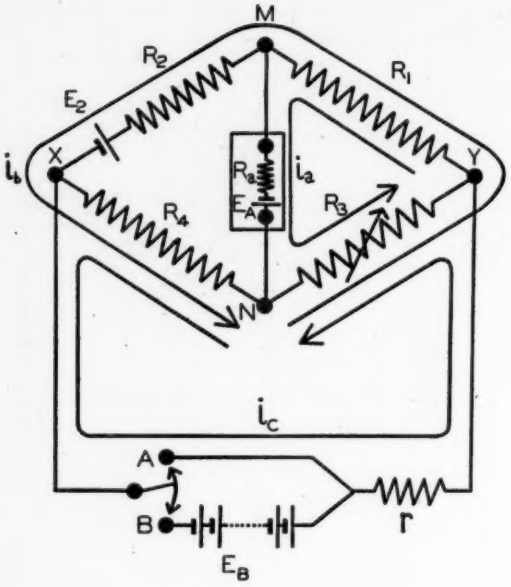

FIG. 4.

This bridge was also used to measure the resistance of the capillary R_2 with the solution flowing through under pressure and hence with a streaming potential E_2 on the electrodes. To do this an experimental procedure was devised which enabled us to adjust R_3 so that the condition $R_2R_3=R_1R_4$ was satisfied, and to have a suitable criterion that this condition is fulfilled.

In presenting the solution to this problem, it should first be noted that the amplifier, when adjusted properly, creates a counterelectromotive force which is equal and opposite to the potential difference across the detector arm, and which reduces the current i_a in this arm to zero within the limit of sensitivity of the instrument. The maker of the instrument states that a current of 10^{-13} ampere is detectable. When the amplifier is developing the counterelectromotive force to oppose the potential difference between M and N (see Fig. 4), a certain response of the sensitive galvanometer attached to the instrument is observed. If this response is identical both without and with the battery potential E_B imposed on the bridge, then the condition $R_2R_3=R_1R_4$ is fulfilled.

To establish this, consider the bridge (Fig. 4) with E_B imposed, with the switch AB in position B. The resistance between X and Y in the battery line is designated as r. Let the current flowing in the various arms of the bridge be considered to be composed of the current components i_a, i_b, i_c, as indicated in Fig. 4. Thus, for example the current flowing through R_3 from N to Y is equal to $(i_a+i_b-i_c)$. The following equations describe the system:

$$i_a(R_1+R_a+R_3)+i_b(R_1+R_3)+i_c(-R_3)=E_A, \quad (5)$$

$$i_a(R_a)+i_b(-R_4-R_2)+i_c(R_4)=E_A-E_2, \quad (6)$$

$$i_a(R_1)+i_b(R_1+R_2)+i_c(r)=E_2+E_B. \quad (7)$$

Solving for i_a

$$i_a=\frac{\begin{vmatrix}(E_A) & (R_1+R_3) & (-R_3)\\ (E_A-E_2) & (-R_4-R_2) & (R_4)\\ (E_2+E_B) & (R_1+R_2) & (r)\end{vmatrix}}{\begin{vmatrix}(R_1+R_a+R_3) & (R_1+R_3) & (-R_3)\\ (R_a) & (-R_4-R_2) & (R_4)\\ (R_1) & (R_1+R_2) & (r)\end{vmatrix}}. \quad (8)$$

However, since no current flows through the amplifier, $i_a=0$, and therefore the determinant in the numerator is equal to 0.

$$\begin{vmatrix}(E_A) & (R_1+R_3) & (-R_3)\\ (E_A-E_2) & (-R_4-R_2) & (R_4)\\ (E_2+E_B) & (R_1+R_2) & (r)\end{vmatrix}=0. \quad (9)$$

Then solving for E_A,

$$E_A=\frac{[R_1(R_3+R_4)+r(R_1+R_3)]E_2 +(R_1R_4-R_2R_3)E_B}{(R_1+R_2)(R_3+R_4) +r(R_1+R_2+R_3+R_4)}. \quad (10)$$

It is evident from Eq. (10) that if the resistance of R_3 is adjusted so that $R_1R_4-R_2R_3=0$, then the value of E_A is independent of E_B. That means that E_B could have its usually high value, or be short-circuited or reversed without any effect on E_A. This gives a criterion to determine the proper bridge balance. In practice R_3 must be adjusted until the value of E_A becomes independent of E_B. It is also possible to show that if $R_1R_4-R_2R_3=0$, then Eq. (10) can be simplified by the rigid algebraic transformation into

$$E_A=\frac{(R_1+R_3)E_2}{R_1+R_2+R_3+R_4}=\frac{R_1E_2}{R_1+R_2}. \quad (11)$$

Here r has been eliminated, which means that the change in the resistance in the battery line between X and Y when the battery is short-circuited does not influence the ratio between E_A and E_2. It also means that the switch AB need not even be closed to short-circuit X and Y, but need only be opened from position B, to give an open circuit which is equivalent to path XAY with very great r. Furthermore, it is apparent from Eq. (10) that when the battery circuit is opened, $E_B=0$, the value of E_A is extremely insensitive to variations in R_3 because R_3 appears only as part of a sum containing much larger quantities. Experimentally this means that the first step is to open AB and then adjust the thermionic amplifier until the galvanometer gives zero deflection for the particular value of E_A, which is equal and opposite to the potential difference between M and N. Then the battery E_B is applied and R_3 adjusted to give the same value of E_A, as shown by zero galvanometer deflection without change in the amplifier adjustment. If E_B is made large enough (4–250 volts depending upon the concentration of solution used) the E_A becomes sufficiently sensitive to variations in R_3 to give the desired precision in the setting and hence in the computed value of R_2. In the general case, the adjustment of the variable resistance R_3 so as to make $R_1R_4=R_2R_3$, is necessary to make the galvanometer read zero both when E_B is imposed and when the battery circuit is open, but in practice with the bridge described, E_A was essentially independent of the value of R_3, since $R_3 \ll R_4$, so that adjustment of R_3 was necessary only when E_B was imposed, facilitating rapid balancing of the bridge.

CLEANING OF CAPILLARIES

To obtain definite and characteristic zeta-potentials, dependent solely on the nature and concentration of the solution under investigation and on the nature of the solid phase, and independent of the previous history of the tube; it is necessary to have the capillary surface free from all adsorbed impurities remaining from previous use of the tube, particularly from multivalent ions, which may greatly modify the surface electrical properties. This is difficult to accomplish, as multivalent ions are probably more strongly adsorbed than univalent ions. With the improved technique of measurement described above the reproducibility of the capillary surface is the greatest source of uncertainty in the zeta-potential measurements. Numerous authors have recognized this difficulty, and have recommended various procedures for cleaning the surfaces. Freundlich and Ettisch[18] have stated that treatment with nitric acid and subsequent rinsing with water is sufficient to remove thorium ions, which are among the most strongly adsorbed, and Kruyt and van der Willigen,[19] and Elissafoff[20] found that chromic acid apparently had the same result. White, Urban, and Krick[15] reported that chromic acid generally caused a 20 percent lowering in the streaming potential values, and found that washing with hot water and steam, and then heating their capillaries to dull redness was superior to other methods. They were not successful in obtaining reproducible streaming potential values, however. There seems to be little agreement among these and other authors, and no decisive results are in the literature, regarding methods of cleaning the capillary surfaces.

A vigorous but completely volatile cleansing agent was used preceding each series of measurements on a solution to be studied. The volatility of the cleaning solution was important, as it permitted a strong presumption that any traces left after rinsing with conductivity water can be removed by heating to a dull redness. Then by preventing contamination by a non-volatile substance except the potassium chloride being measured, it was hoped that a clean surface could be maintained until these measurements were completed. These data would afterwards be available as a norm for comparison with results of future studies involving methods of freeing the surface from undesired adsorbed ions.

Therefore, preceding a series of measurements, boiling aqua regia, made from c.p. nitric and hydrochloric acids, was drawn through the capillaries for a period of hours, followed by hot conductivity water for an equal period. The capillaries were heated to near redness before installing in place with a stream of steam passing

[18] H. Freundlich and G. Ettisch, Zeits. f. physik. Chemie **116**, 401 (1925).
[19] H. R. Kruyt and P. C. van der Willigen, Kolloid Zeits. **45**, 307 (1928).
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TABLE III. Measurements on 10^{-3} N KCl solutions.

Flow	P cm of Hg	E Millivolts	R $\times 10^{-3}$	κ $\times 10^{6}$	$E\kappa/P$ $\times 10^{5}$	ζ Millivolts
$L \rightarrow L'$	31.79	250.7	0.5879	147.85	11.659	−112.6
$L \rightarrow L'$	31.69	250.1	0.5882	147.76	11.661	−112.7
$L \leftarrow L'$	31.32	246.4	0.5879	147.85	11.631	−112.4
$L \leftarrow L'$	31.26	246.0	0.5879	147.85	11.634	−112.4
$L \rightarrow L'$	23.14	182.5	0.5879	147.85	11.661	−112.7
$L \rightarrow L'$	23.06	181.8	0.5879	147.85	11.656	−112.6
$L \leftarrow L'$	23.03	180.7	0.5879	147.85	11.600	−112.1
$L \leftarrow L'$	22.95	180.5	0.5879	147.85	11.628	−112.3
				Av.	11.641	−112.5

through them. As will be seen later, however, this procedure was not wholly successful in solving the problem of reproducibility of the surfaces, even though they were presumably free from impurities at the start. The other parts of the apparatus were thoroughly cleaned with hot nitric acid, except for the electrodes, and leached with hot conductivity water. The electrodes were cleaned with nitric acid before forming the silver-silver chloride mixture on the platinum wire, and afterward were leached in conductivity water for several days before use. Care was taken to keep all sections free from impurities at all times.

MEASUREMENTS ON SOLUTIONS OF POTASSIUM CHLORIDE

Since Langmuir's argument applies to solutions between the range of pure water and $0.001N$, the zeta-potentials created by solutions of concentrations 10^{-3}, 10^{-4}, $10^{-5}N$ KCl were measured. Solutions were made up gravimetrically from recrystallized KCl and conductivity water of specific conductance less than 0.6×10^{-6} mho cm^{-1} when freed from CO_2. They were made and stored in non-sol glass bottles which had been steamed with nitric acid and conductivity water, and leached with the latter for days prior to use. Reservoir L was filled directly from the storage flask, and the various sections of the apparatus joined together. Filtered carbon dioxide-free air, saturated with water vapor, was then passed into L' under a slight pressure, and bubbled slowly through the solution for twelve hours or longer to remove carbon dioxide from the solution. Then pressure from the nitrogen tank was used to force half the solution into L' to equalize the levels. All measurements were made at 25°±0.03°.

In measuring the zeta-potential, the usual procedure was to apply a pressure difference between the reservoirs L and L', then (1) to measure the electrical resistance R_2 of the solution while flowing in the capillary, according to the method developed above; (2) to measure the streaming potential E and the pressure P producing it; (3) repeat (2); and (4) repeat (1). Then the direction of flow was reversed under approximately the same pressure difference, and the four steps above repeated. This procedure was then repeated at different pressures, yielding several sets of data at different values of the streaming potential. By reversing the direction of flow at each pressure, any asymmetry of the electrodes, which may have developed during the course of the measurements, was immediately evident, as it would cause a deviation of the ratio E/P from the average which depended on the direction of flow. This was owing to the fact that such a potential would be algebraically additive to the streaming potential, causing E/P with flow in one direction to be higher than it would be with flow in the opposite direction.

Experience soon showed that with 10^{-3} N and with 10^{-4} N solutions, it was unnecessary to measure the conductance at each pressure, as it was essentially constant over the period during which the set of measurements were obtained, and measurement before and after the set were

TABLE IV. Measurements on 10^{-4} N KCl solutions.

Flow	P cm of Hg	E Millivolts	$E\kappa/P$ $\times 10^{-4}$	ζ Millivolts
$L \rightarrow L'$	31.52	2829.0	13.83	−133.6
$L \rightarrow L'$	31.49	2829.0	13.84	−133.8
$L \rightarrow L'$	31.49	2829.0	13.84	−133.8
$L \leftarrow L'$	31.47	2829.0	13.85	−133.8
$L \leftarrow L'$	31.52	2829.0	13.83	−133.6
$L \leftarrow L'$	31.58	2829.0	13.80	−133.4
$L \rightarrow L'$	25.49	2289.0	13.84	−133.8
$L \rightarrow L'$	25.49	2289.0	13.84	−133.8
$L \rightarrow L'$	25.49	2289.0	13.84	−133.8
$L \leftarrow L'$	25.48	2289.0	13.84	−133.8
$L \leftarrow L'$	25.50	2289.0	13.83	−133.6
$L \leftarrow L'$	25.55	2289.0	13.81	−133.4
$L \rightarrow L'$	20.37	1830.0	13.84	−133.8
$L \rightarrow L'$	20.38	1830.0	13.84	−133.8
$L \rightarrow L'$	20.38	1830.0	13.84	−133.8
$L \leftarrow L'$	20.34	1830.0	13.86	−134.0
$L \leftarrow L'$	20.39	1830.0	13.83	−133.6
$L \leftarrow L'$	20.41	1830.0	13.82	−133.5
			Average	−133.6
			Average deviation	0.08%

sufficient. With 10^{-5} N solutions, however, the more elaborate procedure was necessary, as a certain amount of random variation in the conductance was observed. The cause of this remained unknown, and no amount of mixing would eliminate the effect, so it could probably not be attributed to inhomogeneity of the solutions.

More than fourteen hundred measurements of zeta-potentials have been made, not counting numerous preliminary measurements made during the period when the apparatus and experimental procedures were being developed and tested. The most feasible way to present this mass of data seems to be to give first the details of a typical series of measurements on each of the three concentrations used, namely 10^{-3}, 10^{-4}, and 10^{-5} N KCl. These examples will indicate the precision attained in the actual measurements of E, P, κ, and the zeta-potentials computed from these data for a series of measurements made in rapid succession on a particular solution and capillary. Then we will give a summary of the results of many such series showing the variability of the zeta-potentials for a period of several weeks and the reproducibility of the zeta-potentials on different capillaries and the influence of the previous history of the capillary and of the methods of cleaning used.

A series of results on a 10^{-3} N KCl solution in the smaller capillaries is given in Table III, giving a value of $\zeta = -112.5$ millivolts and a "probable error" of 0.05 millivolt. However, a critical examination of these results shows that the four measurements with flow from left to right give -112.65 ± 0.02, and the four with flow in the opposite direction give -112.30 ± 0.05. This indicates an asymmetry, presumably owing to a slight difference in the potentials of the two electrodes used. This asymmetry is eliminated by averaging the results. The four results using a pressure of 31+cm give -112.52, whereas the four using a pressure of 23+cm give -112.42. The value of R remained essentially constant during this series. The resistance was 587.9 megohms.

In Table IV we give a series of results obtained on a 10^{-4} N KCl solution in the smaller capillary. These data, which were obtained near the end of the work, are exceptionally good but are selected to show the precision attainable after the apparatus and technique had been perfected. Here

TABLE V. Measurements on 10^{-5} N KCl solutions.

Flow	P cm of Hg	E Millivolts	R $\times 10^{-9}$	$\kappa \times 10^6$ (mhos/cm)	$E\kappa/P$ $\times 10^4$	ζ
$L \rightarrow L'$	11.49	7461	10.57	2.210	14.35	−138.6
$L \rightarrow L'$	11.42	7411	10.56	2.213	14.36	−138.7
$L \leftarrow L'$	10.76	7231	10.53	2.220	14.92	−144.2
$L \leftarrow L'$	10.76	7231	10.53	2.220	14.92	−144.2
$L \leftarrow L'$	18.16	11992	10.46	2.234	14.73	−142.3
$L \leftarrow L'$	18.24	12062	10.46	2.234	14.77	−142.7
$L \rightarrow L'$	18.10	11832	10.34	2.259	14.77	−142.7
$L \rightarrow L'$	17.90	11512	10.35	2.257	14.51	−140.2
$L \leftarrow L'$	15.47	10354	10.52	2.222	14.87	−143.7
$L \leftarrow L'$	15.46	10344	10.52	2.222	14.87	−143.7
$L \rightarrow L'$	15.43	10244	10.36	2.255	14.97	−144.6
$L \rightarrow L'$	15.28	9914	10.36	2.255	14.63	−141.4
					Average	−142
					Average deviation	1.2%

TABLE VI. Zeta-potentials (millivolts) with 1.000×10^{-3} N KCl.

Series	Capillary	Time	No. of determinations	κ ($\times 10^6$)	E/P (Av.)	ζ	Av. deviation
A	II	6 days	4	1.5098	7.432	−108.4	0.2%
	II	8	8	1.5063	7.513	−109.4	0.2
	II	10	8	1.5098	7.520	−109.7	0.3
B	I	1	7	1.5052	6.987	−101.6	0.3
	I	4	6	1.5084	7.681	−112.0	0.4
	I	5	8	1.5082	7.728	−112.7	0.3
	I	5	8	1.5082	7.755	−113.0	0.2
	I	6	8	1.5094	7.766	−113.2	0.3
	I	6	6	1.4848	7.717	−110.7	0.3
	I	8	8	1.4848	7.755	−111.2	0.1
	I	11	12	1.5059	7.762	−112.9	0.2
C	I	1	7	1.5077	7.318	−106.6	0.3
	I	1	4	1.5089	7.387	−107.7	0.1
	I	2	8	1.5108	8.145	−118.9	0.1
	I	3	21	1.5080	8.278	−120.6	0.3
	I	5	20	1.5084	8.317	−121.3	0.2
	I	6	12	1.5091	8.382	−122.2	0.2
D	II	0	32	1.5107	8.28 to 8.75	−120.9 to −127.7	
	II	0.5	12	1.5107	8.823	−128.8	0.1
	II	1	12	1.5159	8.804	−129.0	0.2
	II	1	13	1.5133	8.881	−129.9	0.2
	II	2	12	1.5133	8.915	−130.3	0.03
	II	2	17	1.5159	8.888	−130.1	0.2
	II	6	11	1.5124	8.887	−129.9	0.03
E	I	0	26	1.5162	8.310	−121.7	0.3
	I	1	13	1.5171	8.308	−121.7	0.1
	I	7	17	1.5164	8.231	−120.6	0.1

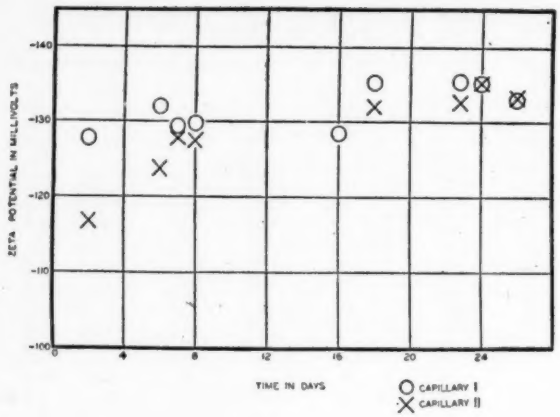

FIG. 5.

there is no difference between the results with variation in the pressure from 20.4 cm of Hg to 31.5 cm of Hg. The average zeta-potential when the flow was from left to right is −133.8 millivolts; and when the flow was in the opposite direction, the result was −133.6 millivolts. The resistance varies from 5646 megohms to 5637 megohms, giving a specific resistance of $\kappa = 15.41 \times 10^{-6}$.

Table V gives a similar series of measurements on a 10^{-5} N KCl solution. These data were obtained with the larger capillary. For this dilute solute the streaming potential was about 12 volts with a driving pressure of 18 cm of mercury. The resistance was more than 10^{10} ohms. The results are more erratic than for the more concentrated solutions used. There is no systematic variation in potential with variation in pressure and the asymmetry amounts to about 1.5 percent.

These three tables were selected as examples of the sort of experimental results obtained. They show that the technique for the actual zeta-potential measurements was apparently reliable to a few tenths of a millivolt. However, it soon became evident that constancy and reproducibility of the zeta-potentials was much less satisfactory. In the following tables the results of more than 1400 individual measurements are summarized. We give the average values of each series of measurements made in rapid succession, together with the number of separate measurements and the average deviation from this average. The Roman numeral I indicates that the set of measurements so designated was obtained with the capillary of 0.032-cm diameter, and cell constant $l/a = 23{,}365$; and II refers to measurements obtained with the capillary of 0.017-cm diameter, and cell constant $l/a = 86{,}920$. These data are given in the chronological order in which they were obtained. The "Time" indicates the number of days elapsed since the solution and capillary first came in contact after assembly of the apparatus.

The first zeta-potentials obtained with 0.001,000N KCl solution after the experimental technique had been developed are shown in Table VI, series A, B, and C.

Between each series of measurements the apparatus was dismantled, the capillary cleaned as described above and refilled. It was observed that the zeta-potential of the freshly cleaned capillary surface increased (in absolute value) over a period of many days, presumably approaching an equilibrium value. Earlier preliminary measurements gave much similar experience. This increase was usually irregular and appeared to be a function of time and of amount of previous flow of the solutions through the capillary. It could sometimes be hastened by warming the capillary gently. It was thought that the slow rise was due to a gradual approach of the silica-solution interface to equilibrium with the solution, due possibly to slow adsorption of ions or hydration

TABLE VII. Zeta-potentials (millivolts) with 1.000×10^{-4} N KCl.

Time (days)	Number of measurements	κ ($\times 10^5$)	E/P (av.)	ζ	Average deviation
		Capillary I			
2	8	1.5708	84.21	−127.8	0.5%
6	7	1.5645	87.30	−132.0	0.3
7	15	1.5645	85.62	−129.5	0.1
8	12	1.5643	85.88	−129.8	0.2
16	17	1.5771	84.34	−128.5	0.5
18	9	1.5685	89.26	−135.3	0.4
23	18	1.5709	89.21	−135.4	0.5
24	20	1.5722	88.95	−135.1	0.6
26	16	1.5709	87.63	−133.0	0.5
		Capillary II			
2	5	1.6089	75.16	−116.8	0.3%
	8	1.5941	76.31	−117.5	0.2
6	17	1.5811	81.03	−123.8	0.3
7	12	1.5863	83.47	−127.9	0.4
8	14	1.5793	83.59	−127.5	1.0
18	9	1.5837	86.29	−132.1	0.7
23	18	1.5407	89.78	−133.6	0.1
24	17	1.5576	89.77	−135.1	0.2
26	20	1.5454	89.18	−133.1	0.3

of the surface layer of silica molecules. If this were so, there ought to have been some effect on the initial and none, we hoped, on the final value of the zeta-potential, if the interface were thoroughly saturated with KCl in $N/10$ solution before the measurements were made with 10^{-3} N solution. This would have meant that initially the interface, instead of being in an equilibrium condition for pure water as with the thoroughly steamed capillary, was in equilibrium condition with $N/10$ KCl and might reach equilibrium with the 10^{-3} N solution more rapidly from the opposite direction. Accordingly capillary II was exposed to $N/10$ KCl, and then, when installed in the apparatus, yielded the data summarized in Table VI, series D. The value of ζ increased rapidly from -120.8 to -127.8 as shown in the first 32 measurements made immediately after installation. After several days some degree of equilibrium seemed finally to have been attained.

This procedure was repeated for capillary I, as summarized in Table VI, series E, and it was found that the zeta-potentials were not in agreement with Table VI, series D. It was found evident that this had not solved the problem of reproducibility of the equilibrium potentials. This was later confirmed by additional similar experiments.

The data in Table VI demonstrate the variability of the capillary surface conditions, which constitute the major source of uncertainty in the measurements reported here.

We then turned our attention to more dilute solutions. Since control of the condition of the surface was obviously not fully achieved by the technique of previous treatment outlined above, or by any other procedure that was later tried, it was believed that a good value for the zeta-potential could only be obtained by allowing time for the two capillaries simultaneously to approach the same value. When this occurred, it could be presumed that equilibrium had been reached. Therefore, the second apparatus already mentioned was built, and both were operated at the same time. The changes in the zeta-potential were studied, and when the two reached identical values, this was taken as the most probable value for the equilibrium potential. This method was applied to the measurements made using 1.000×10^{-4} N KCl solution, which are given in Table VII and Fig. 5. These data illustrate very well the change with time of the zeta-potential, with the capillary II displaying a regular increase, and the larger capillary I an irregular one. Each figure represents the average of a set of

TABLE VIII. Zeta-potentials (millivolts) with 1.00×10^{-5} N KCl.

Time (days)	Number of measurements	$\kappa(\times10^6)$	E/P (av.)	ζ	Average deviation
		Capillary I			
3	8	2.005	618.9	−119.8	0.5%
4	10	2.047	582.8	−115.3	0.8
5	8	2.063	592.3	−118.1	0.7
8	4	2.175	646.6	−135.8	1.0
	8	2.304	592.8	−132.0	1.6
15	8	2.195	684.7	−145.2*	1.5
	8	2.186	684.0	−144.4*	1.3
16	12	2.233	659.2	−142.2*	1.2
		Capillary II			
3	8	2.547	606.4	−149.3	2.5%
4	10	2.599	577.1	−144.9	0.4
5	8	2.599	579.8	−145.6	0.6
8	10	2.721	535.7	−140.9	1.2
	6	2.860	536.8	−148.3	0.8
15	8	2.916	534.7	−150.6*	1.0
	8	2.882	541.0	−150.6*	0.4
16	12	3.048	509.6	−150.1*	0.7

* In obtaining these values, κ and E/P were measured at the same time and the ζ's were computed for each measurement, and then averaged. All earlier ζ values above were determined by measuring κ before and after a series, and taking the average κ, which was then multiplied by the average E/P and the proper factor to give an average ζ. The later method has the advantage of detecting variations in the conductivity which may and do occur, in the extremely dilute solutions, during a series of measurements.

TABLE IX. Zeta-potentials (millivolts) with 1.000×10^{-3} N KCl.

Time (days)	Number of measurements	$\kappa(\times10^4)$	E/P (av.)	ζ	Average deviation
		Capillary I			
11	8	1.4681	7.818	−110.9*	0.6%
12	12	1.4674	7.847	−111.2*	0.9
13	8	1.4666	7.937	−112.5*	0.7
		Capillary II			
11	8	1.4785	7.784	−111.2*	0.4%
12	12	1.4792	7.867	−112.5*	0.3
13	8	1.4784	7.875	−112.5*	0.2

* In obtaining these values, κ and E/P were measured at the same time and the ζ's were computed for each measurement, and then averaged. All earlier ζ values above were determined by measuring κ before and after a series, and taking the average κ, which was then multiplied by the average E/P and the proper factor to give an average ζ. The later method has the advantage of detecting variations in the conductivity which may and do occur, in the extremely dilute solutions, during a series of measurements.

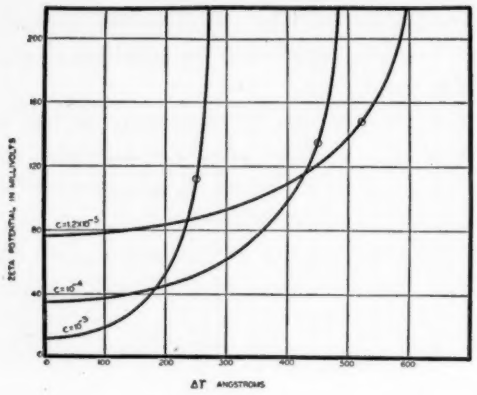

FIG. 6.

measurements made on the stated day after the assembly of the apparatus.

For this concentration, the value of −135 on the twenty-fourth day was chosen as the best value instead of the value of −133 on the twenty-sixth day. It was thought that, other considerations being equal, for KCl solutions the higher value was more probably the correct one. Impurities such as multivalent positive ions or carbon dioxide were found to decrease the magnitude of the zeta-potentials for KCl solutions. Consequently, since the value on the twenty-fourth day was the highest attained simultaneously by both capillaries, it was considered the most probable value of the true equilibrium potential.

The zeta-potentials of the silica in contact with 1.00×10^{-5} N KCl solution were next determined. Table VIII gives the information obtained. The potentials of the two capillaries did not reach identical values, so it was necessary to take the average of the pair nearest each other for the most probable value. These values were −145.2 mv, from capillary I, and −150.6 mv from capillary II, which gave −148 as the average.

Following this, the solution of 10^{-3} N KCl was again put in the apparatus and the zeta-potentials redetermined. The values on the 11th, 12th, and 13th days are given in Table IX. The best value was taken as −112.5 millivolts, which agrees with series A and B, (Table VI), but not with series C, D, and E, (Table VI), the last two having been given a different previous treatment. The results of this last determination were considered to be more reliable than the 5 earlier series.

APPLICATION OF THE LANGMUIR THEORY

The results on zeta-potential measurements recorded above have been used to compute the thickness of the wetting film in accordance with the Langmuir theory. These calculations have been carried out with the rigid forms of the equations given in the paper of Jones and Frizzell.[4] For the sake of abbreviation the development of these equations and the explanation of the symbols are not repeated here. The parameters used in these calculations are taken from a compilation by Birge.[21] The results are shown in Table X. The curve giving the thickness of the wetting film (Δr) as a function of the potential for several concentrations of electrolytes is shown in Fig. 6.

The most dilute solution for which we have as yet succeeded in obtaining zeta-potential measurements is a $0.000,01N$ KCl solution for which we find $\zeta=-148$ millivolts. Using $c=0.000,01$ and $\zeta=-0.148$ gives the thickness of the wetting film $\Delta r=516$ angstroms. Or if we make allowance for the ions derived from water of $c=0.000,002N$ ($c\Lambda=1000\kappa$; $\kappa=0.8\times10^{-6}$, $\Lambda=400$, $c=0.000,002$) giving a total of $c=0.000,012$ the result is $\Delta r=521$ angstroms.

The correcting factor to be applied to the "apparent relative surface tensions" previously reported would then be $r-\Delta r_c/r-\Delta r_0$.

The radius of the capillary in the instrument used by Jones and Ray was $r=0.0136$ cm. Since we do not have zeta-potential measurements for pure water we will tentatively assume that the surface tension for a $0.000,01N$ KCl solution is the same as that of water and estimate the Langmuir correction for $0.0001N$ and for $0.001N$ KCl solutions by reference to $0.000,01N$ KCl in-

TABLE X. Calculation of thickness of wetting films.

c	0.000,01	0.000,012	0.000,1	0.001
m	3.150,48	2.984,40	1.356,20	0.458,48
ψ_m volts	0.080,94	0.076,77	0.034,84	0.011,78
$K=e^{-m}$	0.042,831	0.050,570	0.025,764	0.632,25
$\sin^{-1}K$	2.454,8°	2.898,7°	14.929,9°	39.215,9°
$F\left(\frac{\pi}{2}, \sin^{-1}K\right)$	1.571,5	1.571,8	1.597,9	1.777,3
ζ (volts)	0.148	0.148	0.135	0.112
ϕ	15.808,5°	14.484,4°	8.201,9°	8.187,5°
$F(\varphi, \sin^{-1}K)$	0.275,9	0.252,8	0.143,2	0.143,1
$\frac{1}{\kappa}$	961.85×10^{-8}	878.04×10^{-8}	304.16×10^{-8}	96.185×10^{-8}
Δr (A)	516	521	449	250

[21] R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).

stead of to water. Putting $\Delta r_0 = 521 \times 10^{-8}$ and for Δr_c the values given in Table X give for $0.0001N$ KCl solution

$$\frac{r-\Delta r_c}{r-\Delta r_0} = \frac{0.0136-0.000,004,40}{0.0136-0.000,005,21} = 1.000,05,$$

and for $0.001N$ KCl

$$\frac{r-\Delta r_c}{r-\Delta r_0} = \frac{0.0136-0.000,002,50}{0.0136-0.000,005,21} = 1.000,20.$$

Applying these corrections to the relative surface tension given by Jones and Ray gives for $0.000,1N$ KCl

$$\frac{\sigma_c}{\sigma_0} = 0.999,97 \times 1.000,05 = 1.000,02,$$

and for $0.001N$ KCl

$$\frac{\sigma_c}{\sigma_0} = 0.999,82 \times 1.000,20 = 1.000,02.$$

These results therefore support Langmuir's suggestion that there is no minimum in the surface tension-concentration curve.

However, before reaching a definite conclusion as to the general validity of the Langmuir theory, it seems desirable to secure more zeta-potential measurements for many of the other salts for which we have surface tension measurements, and also to explore the effect of the charge at the air-solution interface, which is ignored in the theory as proposed by Langmuir and used in the above calculations.

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The Fluorescence of Diethyl Pseudo-Isocyanine Chloride in Solution

E. HIRSCHLAFF HUTTEN AND PETER PRINGSHEIM
Department of Physics and Department of Chemistry, University of Chicago, Chicago, Illinois

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The fluorescence and absorption spectra of the dye diethyl pseudo-isocyanine chloride in various solid solutions and at several concentrations and temperatures have been obtained by means of a spectrograph of high dispersion. It has been shown that the dye is fluorescent not only in the polymerized state but also when it is embedded in a "rigid" medium.

I.

IF dyes of the type of pseudo-isocyanine chloride are dissolved in water and if the concentration exceeds 5×10^{-3} molar, the dye begins to polymerize: the viscosity of the solution increases greatly, so that the liquid is transformed into a gel. Simultaneously, a new narrow band appears in the absorption spectrum in the neighborhood of λ5730A, while the broad molecular bands in the green and blue-green region (λ5435A and λ5040A) become weaker.[1] The absorption spectrum of the dye 1,1′-diethyl-2,2′-cyanine chloride, which has been used in our experiments, has been discussed in detail elsewhere.[2] For the sake of brevity the dye will be called "ψ" in the following paragraphs and ψ (10^{-3}), for instance, is used to denote a solution of the dye at a concentration of 10^{-3} molar.

Regarding the emission spectrum of the dye the following facts are known. The ordinary solu-

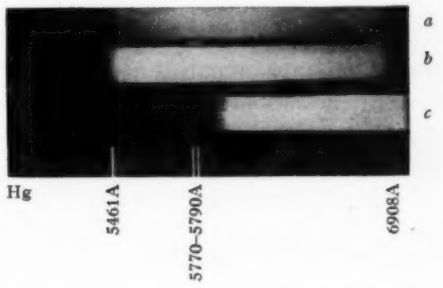

FIG. 1. Fluorescence at −190°C. (a) ψ (10^{-3}) in water +2 g gelatine. (b) ψ (10^{-3}) in pentane. (c) Crystalline dye.

[1] E. E. Jelley, Nature **138**, 1009 (1936); G. Scheibe, Zeits. f. angew. Chemie **50**, 51 (1937).
[2] R. W. Mattoon, J. Chem. Phys. **19**, 268 (1944). For a complete bibliography on the subject we refer to this paper.

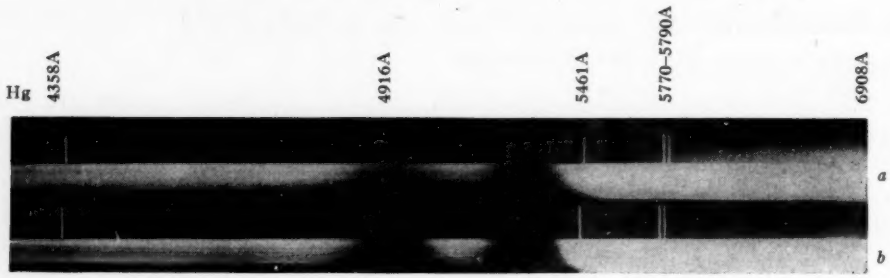

FIG. 2. Absorption of $\psi(10^{-3})$ in glycerol. (a) At 25°C. (b) At −190°C.

tions of the dye in solvents such as alcohol, pentane, etc. and in water (provided that the concentration of the dye is equal to or smaller than 10^{-3} molar) are not fluorescent; these solutions do not form polymers. However, Scheibe found that in concentrated aqueous solutions the polymerized dye exhibits a strong yellow fluorescence. Its spectrum consists of a relatively narrow band which coincides approximately with the so-called *P* band of the absorption spectrum, being slightly shifted in the direction of longer wave-lengths with respect to the latter. The fluorescence can be excited by light absorbed in the *P* band as well as by light of shorter wavelength. While there is no question that the appearance of the *P* band is directly related to the formation of the polymer, it seems probable that the occurrence of fluorescence is due primarily to the fact that the solution changes over into a gel. For it has long been known that many dyes which are not fluorescent in liquid solution become photo-luminescent when they are dissolved in solids or in a gel.

II.

For this reason it appears to be of interest to study the fluorescence of the dye when it is embedded in a rigid medium. In order to obtain a "solid" solution it is possible either to freeze a liquid solution or to mix an aqueous solution with gelatine. At the same time it is important to control the water content of the solutions, since low dye concentration prevents polymerization and, thus, the occurrence of fluorescence in an aqueous solution. The aim of our investigations was therefore to find out whether fluorescence would occur in the "solid" solution when the corresponding liquid solution is non-fluorescent, and to check what influence polymerization has in this case.

All spectra reproduced in this paper were obtained with a Steinheil three prism glass spectrograph of focal length 760 mm. The plates used were Eastman spectroscopic plates I-*F* and II-*F*. A few preliminary spectrograms were taken with the Steinheil spectrograph rebuilt for small dispersion. The exposure times ordinarily varied between a few minutes and one hour.

III.

If a solution of ψ (10^{-3}) in "pure" glycerine is irradiated with light from a carbon arc, a weak reddish fluorescence is emitted. Since this disappears completely when a yellow filter is inserted in the path of the exciting light, the radiation cannot be due to scattered light.

Moreover, the intensity of the fluorescence increases very strongly if the solution is frozen at the temperature of liquid nitrogen. Solutions of ψ (10^{-3}) in ethanol, pentane, and in CCl_4 give very similar fluorescence spectra at a temperature of −190°C, although slight changes in the intensity distribution of the continuous emission band cause some difference in the colour of the fluorescence. Thus the fluorescence of the alcoholic solution is definitely more yellow than the orange-red fluorescence of the glycerol solution.

The fluorescence spectrum of a solution of ψ (10^{-3}) in pentane at −190°C is reproduced in Fig. 1b. It shows a sharp edge near λ5460A and extends with decreasing intensity to about λ6900A. The luminescence persists with weak intensity for several seconds after the primary light has been screened off.

In the main the existence of the fluorescence is not caused by the low temperature but by the

rigidity of the solvent. If a glycerol solution is heated slowly the fluorescence retains nearly its full intensity up to −70°C, at which temperature the solid glass is converted into a viscous liquid; from this point on the intensity of the fluorescence decreases rapidly with increasing temperature.

For the sake of comparison the fluorescence spectrum of the pure crystalline dye is shown in Fig. 1c. The colour of the fluorescence is a deep red; the band extends from 5900A to the long wave-length limit of the sensitivity of the eye and of the photographic plate used. The spectra taken at room temperature and at low temperature do not show any essential difference; no trace of a fine structure appears in the continuous emission band at −190°C.

The absorption spectrum of the glycerol solution at room temperature and at −190°C is shown in Fig. 2. There is no indication of an appearance of the *P* band accompanying the strong fluorescence at low temperature. The molecular absorption bands become a little less diffuse at low temperature but they retain their wave-lengths unaltered; these are somewhat shifted towards the violet as compared with the "molecular" absorption bands of the polymerized aqueous solution published by Mattoon and mentioned in the first paragraph of this paper.

IV.

Solutions of the dye in gelatine-water mixtures were used for the investigation of gels at room temperature. The behavior of these samples depended greatly on the relative concentration of dye and of gelatine in the water and to a certain degree also on the heat treatment which the solutions had undergone.

All solutions were prepared by adding a certain quantity of gelatine to 5 cc of an aqueous solution of ψ (10^{-3}), ψ (5×10^{-4}) or ψ (10^{-4}), etc. In general, the solutions were heated to almost the boiling point in a water bath, and as soon as they appeared to be clear and homogeneous they were allowed to cool down and settle. In a few cases the solutions were only heated to 40°C; these needed more than 24 hours before they became homogeneous. All solutions containing between 0.5 g and 0.05 g gelatine and having a dye concentration of ψ (10^{-3}) became turbid in settling. A solution made with 1 to 2 g gelatine remained quite clear, and solutions containing a dye concentration less than or equal to ψ (10^{-4}) and 0.5 g gelatine remained clear also. Apparently the relative amounts of dye and of gelatine determine whether the dye remains in a molecularly dispersed state (high gelatine content or low dye concentration) or whether the dye molecules coagulate because of polymerization. In the latter case the solution consists of particles of unequal refractive index and therefore becomes turbid.

The absorption spectra of the clear solutions are similar to those of the glycerol solution (Fig. 2) and show only the "molecular" bands of the dye. The solutions are not fluorescent when irradiated with near ultraviolet or blue light except for a faint blue emission band which is characteristic of the pure gelatine. This band extends from the near ultraviolet to the green with a maximum intensity at about 4600A. With increasing dye concentration the fluorescence disappears more and more because of re-absorption by the dye.

The turbid solutions are all fluorescent at room temperature. They exhibit in their absorption spectra, in addition to the molecular bands in the blue-green, narrow bands in the yellow region of the spectrum which evidently correspond to the *P* band of the polymerized dye in water. However, the "*P* band" of the gelatine dye solution is resolved into two components at λ5790A and at λ5710A, respectively. At −190°C these bands become exceedingly sharp (Fig. 3) and are shifted somewhat toward shorter wave-lengths (λ5745A and λ5680A); simultaneously, a much weaker diffuse absorption band appears with its center lying at λ5785A (Fig. 3a). The spectra of Fig. 3 were obtained with a relatively thick layer

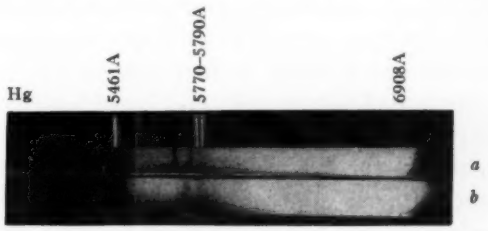

FIG. 3. Absorption of ψ (10^{-3}) in 5 cc H_2O+0.5 g gelatine. (a) At −190°C. (b) At 25°C.

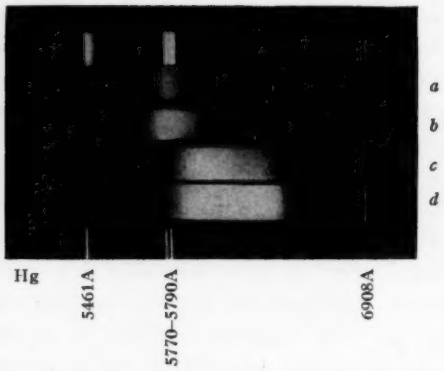

FIG. 4. Fluorescence at 25° C. (a) ψ (10^{-2}) in H_2O, short exposure. (b) ψ (10^{-2}) in H_2O, long exposure. (c) ψ (10^{-3}) +0.2 g gelatine. (d) ψ (10^{-3})+0.5 g gelatine.

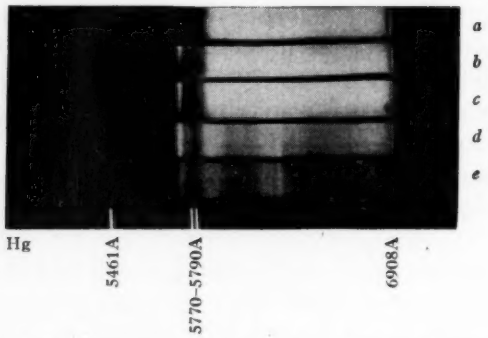

FIG. 5. Fluorescence at −190°C of ψ (10^{-3}) with varying amounts of gelatine. (a) 0.5 g. (b) 0.3 g. (c) 0.2 g. (d) 0.1 g. (e) 0.05 g.

of gel which absorbed all light between λ5460A and λ4800A, i.e., the region of the molecular bands.

The fluorescence spectra of the turbid gelatine solutions at room temperature consist of a band reaching from 5790A to 6320A with an intensity maximum at 6080A. The band is not unlike the *P* band of the polymerized dye in water but is appreciably broader and shifted towards the red, as shown in Fig. 4.

The most unexpected behavior is shown by the fluorescence of the gelatine solution at low temperature. The ψ (10^{-3}) solutions of high gelatine content which are clear and do not fluoresce at room temperature become strongly fluorescent at −190°C; their emission spectrum is very similar to that of the ψ (10^{-3}) solution in pentane (Fig. 1, a and b). The fluorescence emitted by the solution of ψ (10^{-3})+0.5 g gelatine at −190°C extends from 6900A to 5815A; its rather sharp edge at the short wave-length end of the spectrum is shifted by 25A with respect to the same (diffuse) edge of the spectrum of this solution at room temperature. The band occurring at low temperature shows a weak minimum at 6460A (Fig. 5, a), and at the short wave-length end of this minimum (at about 6170A) there appears a narrow band which is just perceptible on the continuous background.

If the gelatine concentration of the solution is decreased further, a greater number of narrow bands appear superimposed on the continuous background and the continuum becomes weaker; a few similar bands show up also on the short wave-length side of the main band. This development reaches its peak at a gelatine content of 0.1 g gelatine in 5 cc of solution. Under these conditions the narrow bands greatly predominate in the emission and a continuum without structure appears only at the far red end of the spectrum (Fig. 5b–e). The wave-lengths of the narrow bands or "lines" are tabulated below (Table I.)

The last strong line beyond the short wave-length end of the continuous part of the spectrum practically coincides with one of the two bands which are found in the absorption spectrum of solutions of this kind (Fig. 3). It is doubtful, however, whether one should pay particular attention to this fact by identifying this line with the *P* band of the fluorescence spectrum of the polymer; rather, it seems to be the last member of a sequence of similar narrow bands extending toward longer wave-lengths. It could be suggested, of course, that the short wave-length edge shown by all fluorescence spectra in Fig. 5 might be the effect of re-absorption of a continuous emission band which is caused by the existence of the strong absorption bands reproduced in Fig. 3. As a matter of fact, the fluorescence of the solution containing 2 g gelatine which does not ex-

TABLE I.

Wave-length	Intensity	Wave-length	Intensity
6260	m sharp	5970	w sharp
6215	w sharp	5895	st
6160	st sharp	5825–5790	v st diffuse (unresolved)
6110	m st diffuse (unresolved)	5750	m st sharp
		5708	v st sharp

Explanation of abbreviations: w: weak; m: medium; m st: medium strong; st: strong; v st: very strong.

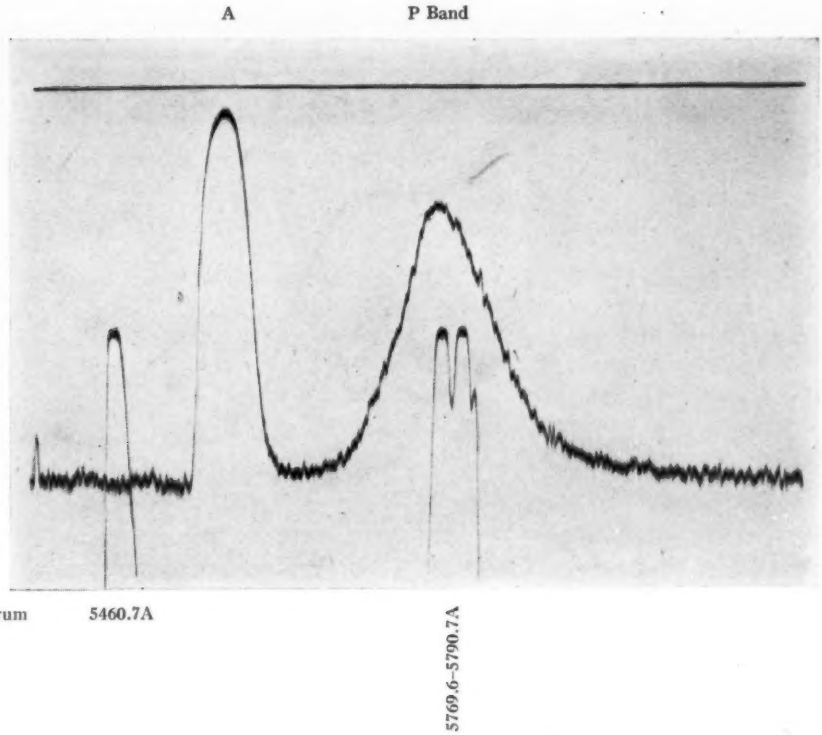

FIG. 6. Photometer curve of *P* band, short exposure.

hibit the yellow *P* band in absorption extends much farther into the green region of the spectrum (Fig. 1a). It is improbable, however, that the absorption should change with decreasing gelatine content. Since the absorption is caused by the dye, after all, it cannot be assumed that the spectral region corresponding to the narrow bands at 5200A and at 5708A is transmitted at a certain gelatine content and that it disappears again at the lower gelatine concentration of 0.05 g.

V.

The *P* band in the fluorescence spectrum of the polymer in water at 25°C has been recorded here photographically for the first time under high dispersion (Fig. 4, a and b). It may be mentioned in this connection that this *P* band is not quite as narrow as it appears when viewed through a direct vision spectroscope. With an exposure of short duration it has an apparent half-width of about 50A and is nearly symmetrical with respect to its center at 5790A (see photometer tracing Fig. 6, corresponding to Fig. 4a). However, a spectrogram of longer exposure reveals that while the short wave-length edge is fairly sharp, the band tails off towards the red beyond 6150A and even exhibits a weak secondary maximum at 6050A (see photometer curve Fig. 7).

As far as its spectral intensity distribution is concerned the *P* band in the fluorescence spectrum of ψ (10^{-2}) in water is independent of the wave-length of the exciting light. A series of spectra was taken with excitation by light of various wave-lengths which were selected from the radiation of a carbon arc by means of a monochromator. By changing the setting of the monochromator and thus the wave-length of the exciting light, the intensity of the fluorescence was altered. The relative intensity distribution, however, remained unchanged and identical with that obtained by irradiating the solution with the line 3655A of the mercury arc. Starting from shorter wave-lengths the intensity of the fluorescence increased gradually with increasing wave-length of the exciting light until it reached a maximum for a wave-length slightly shorter than that corresponding to the *P* band in emission. The band (*A*) shown in the photometer tracing of Fig. 6 is due to the exciting light which was

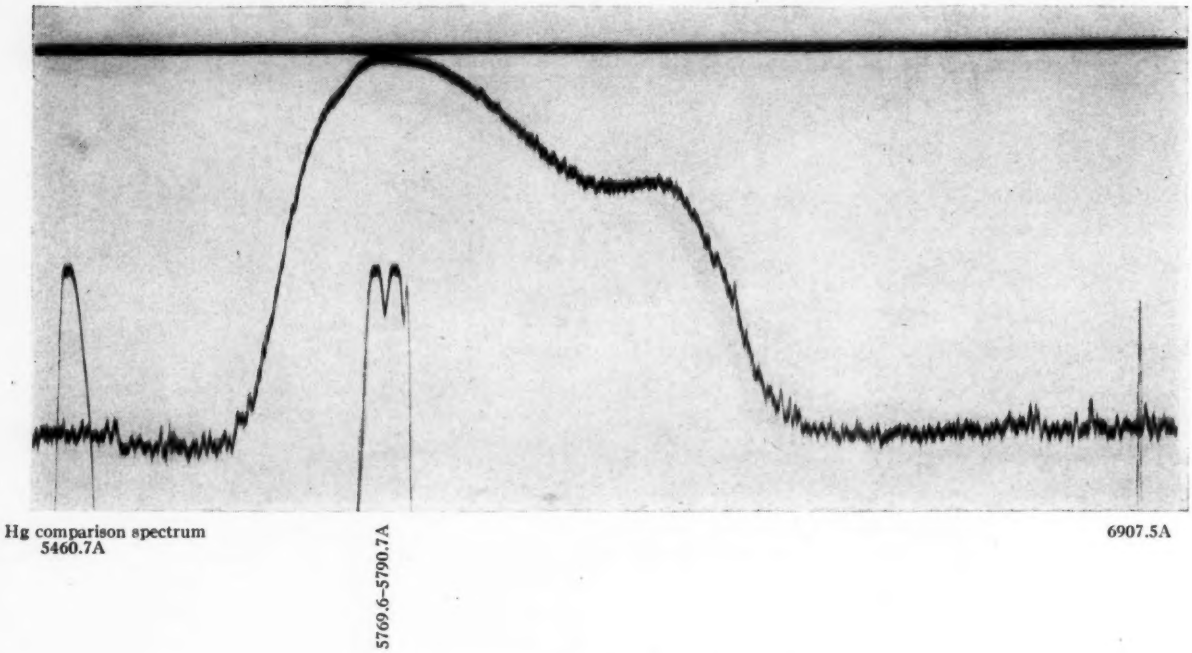

FIG. 7. Photometer curve of P band, long exposure.

scattered at the surface of the dye solution and thus entered the spectrograph; this band (A) corresponds closely to the wave-length producing the strongest fluorescence. When the wave-length of the exciting light coincided exactly with that of the fluorescence, the latter became appreciably weaker, and its intensity rapidly dropped to zero when the monochromator was set for light of still longer wave-length.

A solution of ψ (10^{-3}) in water free of gelatine, which does not fluoresce at room temperature, shows a fairly strong fluorescence at $-190°$C. On the whole the spectrum shows the same structure as that produced by the emission of a solution containing 0.05 g gelatine. But now the lines of wave-length shorter than 5790A are missing completely while the band 5825 – 5790A still possesses a considerable intensity (Fig. 8b).

If an aqueous solution of ψ (10^{-2}), which emits the yellow P band at room temperature, is immersed in liquid nitrogen, the color of its fluorescence changes from yellow to red. The spectrum again has a structure similar to that of the gelatine solution. In this case, however, even the diffuse band 5825A – 5790A (which coincided very nearly with the P band) is completely missing, and the line 6160A has become the predominant feature of the whole spectrum. Furthermore, the continuous part of the emission in the red region of the spectrum is appreciably enhanced, thus causing the change in color mentioned above (Fig. 8a).

VI.

The following are the main results of our experiments:

(1) The fluorescence of ψ is not necessarily connected with the appearance of the P band in the absorption spectrum, which usually indicates the formation of polymers. It can be produced also if the free mobility of the molecules is inhibited to a certain extent by embedding them in a "rigid" medium.

(2) The fluorescence of ψ in viscous and glassy media consists of a broad continuous band in the red and orange region of the spectrum.

(3) Colloidal solutions of ψ in gelatine-water systems are fluorescent at room temperature only for certain relative concentrations of the dye and of gelatine; the spectrum of the fluorescence bears some resemblance to the P band but the emission band is broader, in general, and is shifted toward longer wave-lengths.

(4) If solutions of ψ in gelatine-water which are

fluorescent at room temperature (see 3) are cooled down to the temperature of liquid nitrogen, their spectrum extends much farther towards the red. Moreover, it is split up, especially at low gelatine concentration, into a sequence of narrow line-like bands, the longest of which nearly coincides with the *P* band.

(5) In observing the fluorescence spectrum of a solution of ψ (10^{-2}) in water which shows the *P* band at room temperature, we find this band to disappear completely at $-190°$C. It is replaced by a sequence of narrow line-like bands in the region of longer wave-lengths.

The continuous fluorescence band characterizing solutions which contain no water almost certainly belongs to the normal non-polymerized dye molecule. The narrow banded spectrum may belong to the polymer; however, a direct connection with the *P* band cannot be established. The energy difference between the *P* band at room temperature and the strongest line at low temperature amounts to about 1050 cm^{-1}. It is very improbable that the polymerized molecules

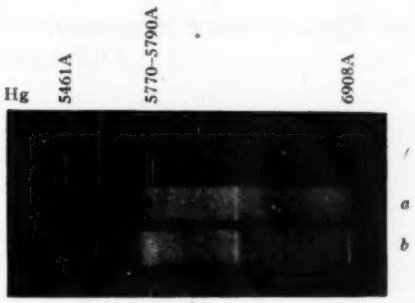

FIG. 8. Fluorescence at $-190°$C. (a) ψ (10^{-2}). (b) ψ (10^{-3}).

are in a state of such high vibrational energy at room temperature. On the other hand, there is no reason to assume that at low temperature the transition from the vibrational ground level of the excited electronic state to a high vibrational level of the electronic ground state should occur with enhanced probability. It is always possible, of course, to imagine a set of potential curves which explain such a behavior, but it does not seem that much advantage can be drawn from such speculations.

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On the Fluorescence Spectra of Naphthacene in Solid Solution of Anthracene for Different Exciting Wave-Lengths

S. C. GANGULY
Indian Association for the Cultivation of Science, Calcutta, India
(Received August 11, 1944)

The fluorescence of green anthracene crystal (naphthacene in solid solution of anthracene) has been studied with exciting light of different wave-lengths and the long wave-length limit for excitation has been found. From the study of the fluorescence and absorption spectra an attempt has been made to interpret the mechanism of the fluorescence phenomenon in this crystal.

INTRODUCTION

THE naphthacene molecule fluoresces brilliantly when it is in the state of a solid solution in anthracene. E. J. Bowen attempted to interpret the mechanism of this fluorescence. Owing to its high brilliance, the fluorescence of this solid solution has attracted the attention of different workers[1] in the field of the study of fluorescence. Naphthacene has both absorption and fluorescence bands in the visible spectrum; its absorption and fluorescence bands remain the same in solid, solution, and vapor states except for a little shift depending upon the medium surrounding the molecule; the absorption and fluorescence bands are like object and image in a mirror. In consideration of the above facts the substance is quite suitable for studying the influence of frequency of the incident radiation. When studying fluorescence, usually ultraviolet light from the Hg arc is used as the source of exciting radiations and by suitable filter the wave-lengths longer than the exciting radiation are cut off. By using incident radiation of this nature, it is therefore not possible to observe the relation between the incident and fluorescent radiation critically. We have used white light as the source of radiation and from its spectrum we have chosen the exciting radiation we wish. This has the advantage over mercury or any other arc spectrum in that we can have any desired wave-length, which may not be available in the arc spectrum.

EXPERIMENTAL

The experimental arrangement for studying the fluorescence bands of the crystal was as follows: The light from a coiled-coil lamp, rendered convergent by a lens, illuminated the slit of the spectrograph. The spectrum was received on a screen with a movable slit. The light passing through the slit was converged by another lens and the crystal was illuminated. The fluorescent light issuing from the crystal together with the exciting light was received by a lens at a suitable angle, and was received on the slit of another spectrograph. The crystal was excited by radiation of wave-length 460, 475, 490 mμ where the first and last are within the absorption bands of the crystal and 475 is in the non-absorbing interval. The spectra were taken under identical conditions. Time of exposures were the same. Photographs were taken on the same plate. The current was kept fairly constant in all the three exposures.

RESULTS

The absorption spectra of the crystal shows a continuous absorption band shorter than 405 mμ, which is owing to anthracene and absorption bands at 435, 460, and 491 mμ which are owing to naphthacene (Fig. 1). The absorption spectra were taken in the usual way. Pure naphthacene absorbs at 425, 453, and 485 mμ. In this crystal naphthacene molecule fluoresces, having the positions of the bands at 498, 533, 574 mμ. By using monochromatic exciting radiation of various wave-lengths, we find the following results.

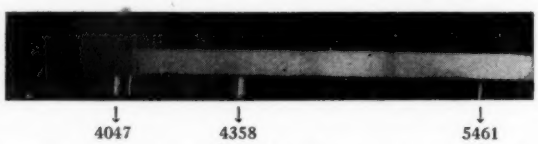

FIG. 1. Absorption spectra of the crystal of anthracene containing traces of naphthacene.

[1] K. S. Krishnan and P. K. Seshan, Acta Phys. Polon. **5**, 289 (1936); E. J. Bowen, Nature **142**, 1081 (1938).

1. The crystal does not give any fluorescence if the incident radiation is of wave-length longer than the longest absorption band of the crystal.

2. The positions and number of the fluorescence bands of naphthacene are independent of the exciting wave-length, as long as the wave-length is not longer than its lowest absorption band.

3. With the change of frequency of the incident radiation, we find a change of intensity of the fluorescence bands; the intensity is greater when the incident light wave is an absorption band of the substance. The change of intensity is practically the same for all the fluorescence bands of the substance (Fig. 2).

4. If the crystal is excited by strong ultraviolet radiation from a Hg arc (3650, 4047A), in addition to the characteristic fluorescence bands of naphthacene we get four more fluorescent bands at 400, 414, 440, 468 mμ which are the characteristic fluorescent bands of anthracene (Fig. 3).

The variable distribution of the energy of the spectrum from which monochromatic beam has been isolated cannot be the reason of the difference of intensity at 460, 475, 490 mμ. The

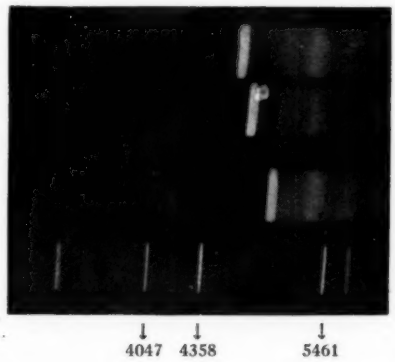

FIG. 2. Fluorescence spectra of naphthacene, excited by λ4910, λ4750, λ4600.

incandescent lamp used had a perfectly continuous spectrum and the difference of intensity between two neighboring points 460, 475, and again between 475, 490 mμ, is not sufficient for the considerable fall of intensity in the first case and considerable rise of intensity in the latter case.

The results are tabulated in Table I.

In order to find the critical wave-length of excitation we have changed the wave-length of the exciting light wave by changing the movable slit of the monochromator. From the plate it is evident that so long as the exciting radiation lies inside the absorption band, its intensity is quite high and as it goes beyond it the intensity is diminished, and when it is well beyond the longest absorption band on the longer wave-length side, no fluorescence is observed (Fig. 4).

The crystal has two long limiting wave-lengths for excitation: one for anthracene and the other for naphthacene. If the exciting radiation lies

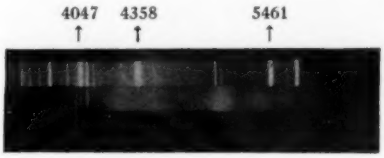

FIG. 3. Fluorescence spectra of the crystal of anthracene containing traces of naphthacene. Excited by λ3650, and λ4047 of the Hg arc.

within the longest absorption band of anthracene, both the fluorescent bands of anthracene and naphthacene are present, but if it is longer than the longest absorption wave of anthracene but shorter than or equal to the longest absorption wave of naphthacene, the fluorescent bands of naphthacene alone are present.

CONCLUSION

That all the fluorescence bands of naphthacene are excited by monochromatic radiation of any wave-length within the longest absorption band of naphthacene is interesting. As the exciting radiation is changed from one absorption band to the other through a non-absorbing interval, we find a change of intensity of the fluorescence bands in accordance with the change of absorption by the substance. We have not measured the intensities of the light emitted and absorbed, but we observe that when the exciting light wave coincides with the absorption band of naphthacene the intensity of fluorescence is increased. Naturally we have reasons to believe that the fluorescence yield depends upon the intensity absorbed. From the above facts and also from the study of its absorption bands we think that the mechanism of fluorescence of naphthacene is as follows: A naphthacene molecule by absorbing light energy is raised to various states of higher energy and all of them come to the lowest

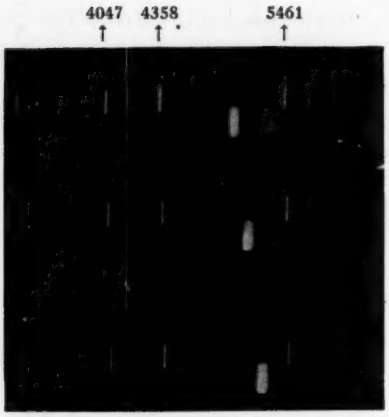

FIG. 4. Fluorescence spectra of naphthacene, excited by different wave-lengths. It shows the long wave-length limit for excitation.

vibrational level of the higher state. All the fluorescence of naphthacene comes from this level which is reached by degradation of electronic and vibrational energy.

Bowen[2] observed brilliant fluorescence of naphthacene in the solid solution of anthracene and compared it with the typical inorganic fluorescent solid such as zinc sulphide in presence of copper, etc. As the absorption bands of anthracene lie on the short wave-length side of those of naphthacene and the two do not overlap, there is reason to believe that in this crystal naphthacence molecules are the activators. Bowen supposed that anthracene molecules after absorbing light energy give it to naphthacene and so naphthacene fluoresces. But our findings that the naphthacene fluoresces quite nicely even when the exciting light wave is longer than the longest absorption band of anthracene, and that the intensity of fluorescence of naphthacene depends only upon the quantity of light absorbed contradict the above suggestion.

It is interesting to note that the intensity of the fluorescence bands is stronger when the wave-length of the exciting radiation is 490 mμ than when it is 460 mμ though both of them are absorption bands of the crystal. From the plate it is evident that extinction coefficient of the absorption band at 490 mμ is larger than that of 460 mμ. These facts qualitatively support the view that the efficiency is independent of exciting wave-length.

TABLE I.

Absorption bands	Relative intensity visual	Exciting radiation	Fluorescence bands	Relative intensity visual
435		460	498, 533, 574	2
460	2	475	498, 533, 574	1
491	3	491	498, 533, 574	3

The author wishes to express his sincere thanks to Professor K. S. Krishnan for suggesting the problem and Professor K. Banerjee for helpful discussion and keen interest taken during the progress of work.

[2] E. J. Bowen, Nature **142**, 1081 (1938).

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

X-Ray Diffraction Study of Micelle Structure in Potassium Laurate Solutions

E. W. HUGHES, W. M. SAWYER, AND J. R. VINOGRAD
Shell Development Company, Emeryville, California
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ISOTROPIC soap solutions have been reported[1] to contain ordered aggregates of micelles which at small and wide angles give x-ray diffraction patterns. The short spacing of 4.4A is independent of the concentration or the chain length of the soap. The long spacing varies from 50 to 125A and depends on the concentration, the chain length, and on the amount of benzene solubilized[2] in the solution. These micelle aggregates are considered to consist of at least five double layers of soap molecules oriented side by side and tail to tail. In the case of sodium oleate, the carboxylate surfaces are separated from each other by water layers 30 to 50A thick, while the tail surfaces may be separated from each other by layers of solubilized benzene up to 40A in thickness.

In a study of the potassium laurate—water—toluene system we have confirmed the previous work in the following points: (1) the long spacing decreases linearly with soap concentration, (2) the increase in long spacing upon addition of hydrocarbon, in this case toluene, is directly proportional to the mole ratio of additive soap, and (3) the long spacing for an 18.3 percent potassium laurate solution is 50.4A compared to a value of 50A quoted by Philippoff.[1g]

The increments in the long spacing resulting from water and toluene additions are, moreover, independent and additive. A set of parallel lines with the mole ratio toluene/soap as a parameter represents the data for the influence of concentration on the long spacing of 13.9 to 25.0 wt. percent potassium laurate solutions. Another set of parallel lines with soap concentration as a parameter is obtained for the same data when long spacing is plotted against mole ratio, toluene/soap. It seems probable then that in these concentration ranges the proportion of soap in the micelle form is not affected by changes in water or toluene content.

The proposed micelle structure is supported by our observations of the changes in line intensities when substances are solubilized. Hydrocarbons, which generally have an electron density of less than 0.30 electron per cubic Angstrom, intensify the line. This is to be expected since they introduce a large periodic negative variation from the average electron density of the micelle. Methylene chloride (e.d.=0.40 e/A^3) produces little change. Bromobenzene (e.d.=0.44 e/A^3) reduces the intensity and eventually renders the line invisible; its positive variation must then balance that produced by the potassium ion—water layer. With bromoform (e.d.=0.78 e/A^3) the same is true at lower concentrations, and enough can be added to bring back the intensity, presumably with a phase shift of 180° in amplitude.

The effect of a solubilized additive upon long spacing depends markedly upon its chemical nature. The change in spacing expressed in Angstroms per mole of additive per mole of soap is plotted against molar volume of the additive in Fig. 1. The paraffin hydrocarbons fall on a straight line extrapolating to an intercept at about 50 milliliters per mole or (4.4A^3) per molecule. A line with 20 percent smaller slope for aromatics extrapolates to approximately the same point. On the basis of the present model, if all the additive simply layered between the ends of the soap chains, the line should begin at the origin; thus a portion of the solubilized additive is absorbed elsewhere, perhaps between the sides of the aliphatic chains in the micelles

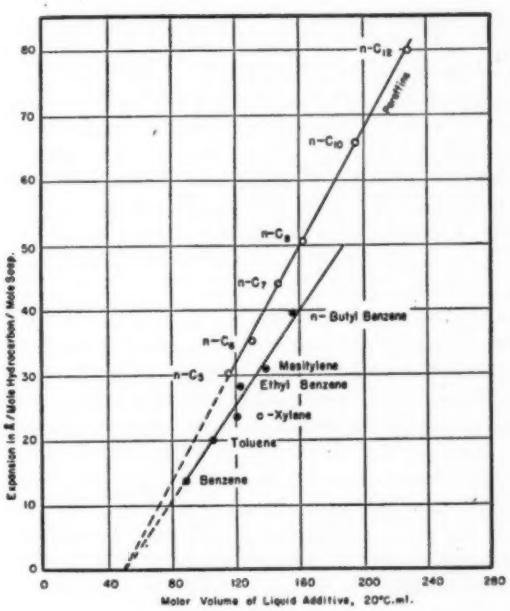

FIG. 1. Expansion of micelle repeat distance by hydrocarbons solubilized in a 22.1 wt. percent potassium laurate solution.

described above, or alternatively within ionic micelles not detected by x-rays.

It has recently been demonstrated that styrene solubilized in soap solutions can be polymerized to form a latex of high molecular weight polystyrene[3,4] and that this reaction constitutes an intermediate step in emulsion polymerization processes.[3] Our results with potassium laurate—styrene solutions reveal that the long spacing first increased by the incorporation of styrene is decreased as a result of

polymerization almost to its original value. These micelles are then capable of solubilizing more styrene and continuing their role in emulsion polymerization.

[1] (a) K. Hess and J. Gundermann, Ber. **70**, 1800 (1937); (b) K. Hess, H. Kiessig, and W. Philippoff, Naturwiss. **26**, 184 (1938); (c) H. Kiessig and W. Philippoff, Naturwiss. **27**, 593 (1939), K. Hess, W. Philippoff, and H. Kiessig, Kolloid Zeits. **88**, 40 (1939); (d) J. Stauff, Kolloid Zeits. **89**, 224 (1939); (e) H. Kiessig, Kolloid Zeits. **96**, 252 (1941); (f) J. Stauff, Kolloid Zeits. **96**, 244 (1941); (g) W. Philippoff, Kolloid Zeits. **96**, 255 (1941).

[2] J. W. McBain in *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1942), p. 99.

[3] J. R. Vinograd, L. L. Fong, G. S. Ronay, and W. M. Sawyer, "Studies in Emulsion Polymerization," presented before the Division of Colloid Chemistry, 108th Meeting of the American Chemical Society, New York, N. Y., September 13, 1944.

[4] W. P. Hohenstein, S. Siggia, and H. Mark, Ind. Rubber World **111**, 173 (1944).

The Intensity and Polarization of Raman Lines

WALTER F. EDGELL
Department of Chemistry, University of Iowa, Iowa City, Iowa
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IN the last few years several attempts have been made to calculate the intensity and depolarization factor of Raman lines in a semi-empirical manner. Thus Rao[1] dealt with the symmetrical valency vibration in CCl_4 on the basis of Silberstein's theory[2] of optical anisotropy in molecules, and Nath and Chalam[3] obtained a value for the ratio of the intensities of the Fermi resonance lines in CO_2 by assuming that bond polarizabilities[4] were functions of bond lengths only. More recently Eliashevich and Wolkenstein[5] have developed this latter idea in a somewhat more general manner. All of these methods involve assumptions which, at best, are only first approximations to reality. Interest has been shown here in this problem for some time and equations have been developed which are more general than any of the above.

On expanding the elements of the polarizability tensor in a Maclaurin's series, one obtains a set of constants which determines the intensity and depolarization of the scattered light.[6] However, if one expands in terms of *internal* coordinates, instead of the normal coordinates, as is customary, these constants will characterize the intensity in the same way that force constants characterize the frequency of vibration (and will be evaluated in the same way). Designating the partial derivative of the mnth element of the tensor with respect to the normal coordinate Q_λ or to the internal coordinate r_k as $A_{mn;\lambda}$ and $A_{mn;k}$ respectively, one has

$$A_{mn;\lambda}=\sum_k A_{mn;k}L_{k\lambda}, \tag{1}$$

in which the $L_{k\lambda}$ are the elements of the transformation matrix from internal coordinates to normal coordinates.

Now expressing the polarizability of each bond in terms of a rectangular coordinate system *fixed to that bond*, it may be shown that[7]

$$A_{mn;k}=\sum_{qij}\left\{S_{qi,m}S_{qj,n}\frac{\partial\alpha_{q;ij}}{\partial r_k}+\alpha^0{}_{q;ij}\frac{\partial(S_{qi,m}S_{qj,n})}{\partial r_k}\right\}, \tag{2}$$

where $\alpha_{q;ij}$ is the ijth element of the polarizability of the qth bond, $\alpha^0{}_{q;ij}$ its value in the equilibrium configuration, and $S_{qi,m}$ is the cosine of the angle between the ith axis of the qth bond and the mth "principal" optic axis of the molecule. This equation represents the generalization of the bond polarizability method and differs from that presented by Eliashevich and Wolkenstein primarily by including the effect of the distortion of the bond electron cloud as a result of the deformation of valence angles. Moreover it does not assume that the bond axes are the principal optic axes of the bond for the deformed molecule.

A further simplification of the last equation (in form at least) is possible without any loss in generality. In certain instances it may be convenient to regard each bond axis system as being fixed in the inertial system formed by the principal axes of the (whole) molecule. Since the deformation of valence angles will not result now in the reorientation of bond axes, the last term in Eq. (2) is zero. The intensity is now dependent only on the $\partial\alpha_{q;ij}/\partial r_k$. It should be remembered that these derivatives now include the effect of reorienting the bond electron cloud as well as its distortion.

Besides the above methods there is another which is not without its appeal. The directions which are basic in a molecule, from the point of view of symmetry, are not so much rectangular directions as bond directions. Recognizing this one can write for the polarizability of the whole molecule

$$\bar{\bar{\alpha}}=\sum_{ij}\bar{u}_i\bar{u}_j\alpha_{ij}, \tag{3}$$

where $\bar{u}_i$ is a unit vector in the direction of the ith bond, the summation is over the pertinent bond directions,[8] and the α_{ij} may be regarded as *characteristic functions*. Thus the polarizability of CH_3Cl may be described by the four quantities α_{ClCl}, α_{HH}, $\alpha_{HH'}$, $\alpha_{HCl}=\alpha_{ClH}$. In terms of these it can be shown that

$$A_{mn;k}=\sum_{ij}S_{im}S_{jn}\partial\alpha_{ij}/\partial r_k. \tag{4}$$

The intensity of Raman lines is now determined by the variation of these "functions" with respect to the internal coordinates.

All the above methods may be considerably simplified in application by taking advantage of the symmetry of the molecule. For if, for instance,

$$\alpha_{ij}=f\{r_k, r_{k'}, \cdots\} \tag{5}$$

then

$$\alpha_{(ci)(cj)}=c\alpha_{ij}=f\{(cr_k), (cr_{k'}), \cdots\}, \tag{6}$$

c being any operation of the point group of the molecule. The resultant equations will be presented in a forthcoming article on this subject.[7] Obvious extensions to other topics as Rayleigh scattering, Kerr effect, infra-red intensities, etc. exist and will be dealt with later.

[1] B. P. Rao, Proc. Ind. Acad. Sci. **11A**, 1 (1940).
[2] L. Silberstein, Phil. Mag. **33**, 92, 215, and 521 (1917).
[3] N. Nath and E. V. Chalam, Proc. Ind. Acad. Sci. **13A**, 339 (1941).
[4] K. G. Denbigh, Trans. Faraday Soc. **36**, 936 (1940); L. N. Wang, J. Chem. Phys. **7**, 1012 (1939) and others.
[5] M. Eliashevich and M. Wolkenstein, Comptus Rendus URSS **41**, 366 (1943). Apparently the ideas expressed in E. and W.'s paper had their origin in several Russian articles by Wolkenstein in 1941 (see reference 1 of E. and W.).
[6] G. Placzek, Handbuch der Rachiologie **6(II)**, 205 (1934).
[7] W. F. Edgell, to be published soon.
[8] A slight modification is obviously required for planar or linear molecules.

Intensity and Polarization of Raman Lines and the Form of Molecular Vibrations

WALTER F. EDGELL
Department of Chemistry, University of Iowa, Iowa City, Iowa
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IN a recent paper on this subject, Eliashevich and Wolkenstein[1] assume that the "polarizabilities of individual bonds" are functions of the bond distances only, and hence they are independent of changes in the valence angles. As shown by these authors, it follows from this assumption that "Raman lines due to pure deformation vibrations have, irrespective of their symmetry, a depolarization factor of 6/7." Later on in their article they conclude that "the force constants generally referred to in the literature have usually little to do with reality, notwithstanding good agreement between calculated and measured frequencies."

These statements have such far-reaching consequences that it seems worth while to examine them in greater detail. With regard to the first it is quite true that the so-called symmetrical "deformation" vibration of the CH_2 group usually has a relatively large value of the depolarization factor. However, this is not universally true of all symmetrical "deformation" vibrations. For example the "deformation" vibration in $CHCl_3$ (A_1 representation) has a depolarization factor of $\rho = 0.18$. In fact the depolarization factor of the corresponding vibration in all the haloforms has similarly low values. Now, of course, these are not *pure* deformation vibrations; it is doubtful if such *ever* exist. It seems that one is on uncertain ground in assuming *a priori* that the low value of the depolarization factor in this case is due alone to the presence of some carbon-halogen stretching motion in the deformation vibration and not at all due to dependence of the bond polarizabilities upon the deformation of the valence angles involved in this vibration. A normal coordinate treatment of chloroform[2] indicates that there is somewhat more coupling between the carbon-chlorine stretch and the valency angle deformation than is present for instance in methyl chloride. True this calls for an increase in the participation of the carbon-chlorine stretch in the "deformation" vibrations; yet it simultaneously indicates the increased importance of the dependence of the bond polarizabilities upon the valence angles. For if the force required to increase the carbon-chlorine separation by unit distance depends upon the valence angles, will not the force (electric intensity) required to induce a unit moment in the carbon-chlorine bond also depend upon the valence angles?

In view of the general lack of quantitative intensity measurements in the Raman effect and the almost nonexistence of data for the gaseous phase, it seems much better to reserve judgment concerning the universal nondependence of bond polarizabilities upon the valence angles until considerably more data are available. Certainly it appears too early to claim for the first of the above statements that "this rule is an extension of Placzek's ($\rho = 6/7$ for not fully symmetrical vibrations)."

The authors of the above article[1] do not explain how they arrived at the second conclusion quoted above. It may be that they were forced to it by difficulties in obtaining agreement between intensities and depolarization factors calculated from these force constants (and bond polarizabilities) and the observed intensities and depolarization factors. Be that as it may, the general validity of this conclusion is yet to be established. The transferability of force constants from molecule to molecule[3] certainly suggests that they have some reality. Perhaps it would be better to consider the form of a fundamental vibration (the normal coordinate) as being essentially that given by the force constants,[4] at least until it has been definitely established that the observed intensity and depolarization factor of Raman lines cannot be accounted for by including the dependence of the bond polarizabilities upon the bond angles as well as upon the bond lengths. One should not let the desire for additivity in the polarizability of a molecule lead one to reject the dependence of bond polarizabilities upon valence angles.

[1] Eliashevich and Wolkenstein, Comptes Rendus URSS **41**, 366 (1943).
[2] W. F. Edgell, "Studies in Molecular Structure" (M.S. thesis), University of Iowa (1941).
[3] B. L. Crawford and S. R. Brinkley, J. Chem. Phys. **9**, 69 (1941).
[4] Of course we refer here to those constants for which valid checks are available either from within or without the molecule.